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Theory of Color of Organic Compounds

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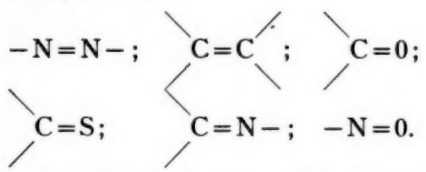
Several structural formulae can be written for a colored compound, since the molecule usually contains an alternation of single and double bonds. The color is attributed to absorption bands corresponding to transitions between the levels which arise from a resonance among these different possible structures. A calculation is made for the levels of benzene, cyclohexadiene, fulvene, and azulene; fulvene being a yellow compound, azulene a blue one; the others, although colorless, have absorption bands in the near ultraviolet. One parameter only enters the calculation and is evaluated by data on heats of hydrogenation. The absorption bands of the molecules are then calculated without using any optical data, the results agreeing well with experiment. The calculation is amplified in the case of benzene so as to include polar structures and also triplet states in the linear combination representing the molecule. The symmetry of the states is discussed in connection with selection rules, which are found to be in agreement with the relative intensity of the band groups in benzene. An interpretation of the structure of the 2600A band is proposed which is shown to account for many properties of this band system.

INTRODUCTION

EXPERIENCE has shown that absorption of visible or near ultraviolet light (>2000A) only occurs when certain groups are present in the molecule. Examples of such groups, called chromophores, are:



It will be noticed that each of these groups possesses an alternation of single and double bonds. In a colored compound these groups occur conjugated with other double bonds as is seen in the molecules of Fig. 1.

Although a colored molecule has many such conjugated double bonds, the color does not depend upon the number of these alternations alone. Fulvene, which is yellow, has three such alternations, whereas diphenyl, which does not absorb in the visible but only in the ultraviolet, has six. The color, then, is very strongly influenced by the way in which the chromophores are bound together; that is, it depends upon the structure of the entire molecule.

The role played by chromophores can be seen from the following qualitative discussion. The alternation of single and double bonds which is present in a chromophore always enables one to write several structural formulae for the molecule; benzene, for instance, may be written five ways (cf. Fig. 2).

When several structural formulae may be written the molecule is not truly represented by any one of them, but behaves somewhat like a mixture of all structures. The true states of a molecule of this kind are, then, not described by one structural formula but are obtained by taking

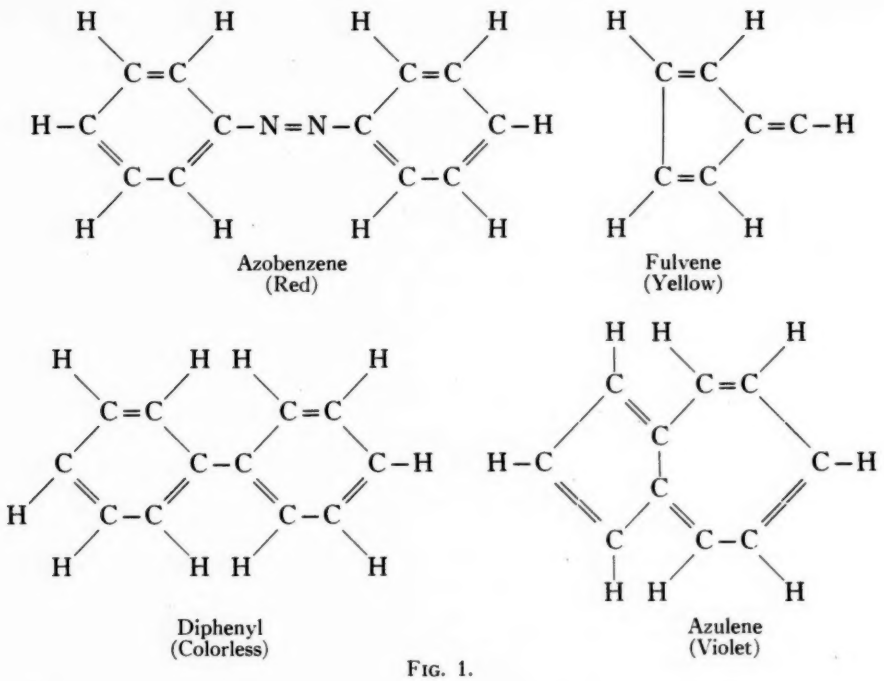


FIG. 1.

all the formulae into account.[1] Although the various structures may have identical or slightly different energies, the actual energy values of the molecule can be entirely different, due to a resonance phenomenon such as occurs in the simple case of two identical coupled pendula. In the case of benzene the two Kekule structures have identical energy, as do the three Dewar structures, the latter three having a higher energy than the former two since a *para* bond is weaker than an *ortho* bond. Now, when we calculate the true energy levels of the molecule (making a number of approximations) we find that the energy levels corresponding to the five structures

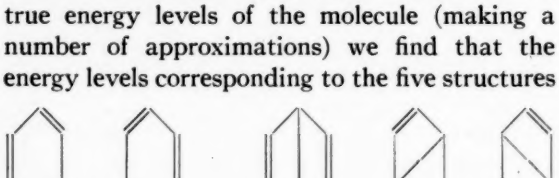


FIG. 2.

have split into five widely separated levels (cf. Fig. 3. The α which appears in the figure is a parameter which will be described and evaluated later[2]).

Now the transitions between these true levels of the molecule will give rise to absorption bands which, within the accuracy of this calculation, lie at the proper frequency. That is, the absorption bands are due to transitions between levels which arise from the resonance between the states corresponding to the different structures.[3]

The electronic transition of lowest energy has been calculated for several organic molecules. Benzene is treated in most detail, and an

[1] E. Hückel, Zeits. f. Physik **70**, 204 (31); L. Pauling and J. Sherman, J. Chem. Phys. **1**, 606, 679 (33).

[2] Two electrons present on neighboring atoms lower the energy of a structure (forbidding resonance between structures) by $-\alpha$ (α is negative) if the electrons are paired so as to form a bond, and raise the energy by $-\frac{1}{2}\alpha$ if they are not paired. The two Kekule structures hence have an energy lowering of $(3-3/2)\alpha=1.5\alpha$ whereas the three Dewar structures each have an energy lowering of $-(2-4/2)\alpha=0$.

[3] The picture of the molecule resonating between different structures and a consequent splitting up of the energy levels is a description of the method of calculation rather than of the fundamental problem. To calculate the color of a molecule one must know the true energy levels of the molecule and the transition probabilities between them. The concept of resonance comes in when we attempt to calculate these levels by describing the molecule by structural formulae, since several formulae may be equally good; for example, the two Kekule forms for benzene. A resonance between these forms does not imply that the molecule changes quickly from one form to the other. The situation is rather that the molecule is in a stationary state in which it is simultaneously partially like each structure. We could avoid the discussion of resonance if as a first-order approximation we solved the problem of an electron moving in a potential field of the symmetry of the nuclei. This latter approach is the essence of the H-M-H method, whereas the resonance picture is the H-L-S-P. Both pictures should approach one another in higher order approximations.

interpretation of its spectrum is given. A calculation of azulene, a compound of physiological interest, points out a rather promising application of a calculation of spectra to physiological problems. The determination of the structure of a natural product, perhaps a hormone, is a matter of many years' work in which many guesses are

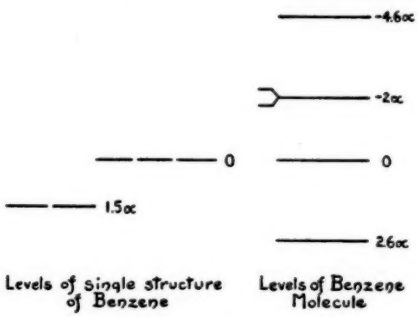
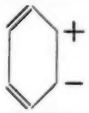


FIG. 3.

made and later rejected. One could calculate the spectrum of a proposed structure, check it against the experimental one, and so keep on the right track.

Since the problem of a complicated molecule is too difficult to solve exactly, we must resort to approximation methods. It is desirable to make a calculation of this sort with several methods based on quite different approximations. The two methods in use are the Hund-Mulliken-Hückel and the Heitler-London methods, the latter extended by Slater and Pauling. The former in its convenient but simplified application (without antisymmetrizing the molecular orbital) neglects the repulsion of the electrons. The latter method overemphasizes this repulsion and assumes that two electrons never pile up on the same atom; that is, writes the wave function for the molecule as a linear combination of the functions representing the structures in which all the atoms are neutral, neglecting ionic terms in the wave function.

In this calculation the H-L-S-P method has given much better quantitative results than the H-M-H. The H-M-H gives the relative spacing of the levels quite well, but not the absolute spacing. All of the quantitative calculations are, therefore, done by means of the H-L-S-P method.[4] It is possible to relieve the overemphasis on electron repulsion of the H-L-S-P method very simply, since it is really not inherent in this method that one consider only those structures which have not more than one π electron on each atom. That is, one may write structures like



as well as those shown in Fig. 2, and include all the structures in the combination of functions which represents the molecule.

Since we are interested in resonance between double bonds in complicated molecules, we can simplify the problem greatly without much loss in accuracy by neglecting all electrons except those forming π bonds. Benzene is thus treated as a six-electron problem. The justification is that π wave functions have a node in the plane of the ring so that the overlap between them and the function for an electron forming a bond in the plane is very small.

We treat a molecule like benzene as follows: Each carbon has three bonds at 120° angles,[5] with the axes of the electron clouds in the plane of the ring (cf. Fig. 4). Now, each carbon has one

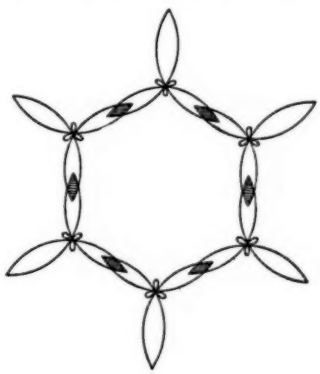


FIG. 4.

more electron whose density cloud is a dumbbell with its axis perpendicular to the plane of the ring (cf. Fig. 5). The clouds of these latter

FIG. 5.

[4] In the following paper the calculation is made with the H-M-H method with good qualitative results.

[5] J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. July 1935, p. 204.

electrons overlap the clouds of the electrons forming in-plane bonds only very slightly.

Method

We first write all possible structures for our molecules, a so-called canonical set. This set is found by using the following theorem of Rumer, Teller and Weyl[6] based on the theory of binary invariants: "Arrange the atoms in a circle which need have nothing to do with the actual arrangement in the molecule; any structure in which no bonds cross is one of the set." The wave function for a structure in which bonds cross can be written as a linear combination of functions involving no crossed bonds.

Now to each structure, k, of the canonical set attach a wave function[7]

$$\Psi^k=\frac{1}{2^{n/2}}\sum_R(-1)^R R\left\{\frac{1}{(2n!)^{\frac{1}{2}}}\sum_P(-1)^P P \times\prod_{l=1}^{n}\psi_{2l-1}(2l-1)\alpha(2l-1)\psi_{2l}(2l)\beta(2l)\right\}$$

$$=\frac{1}{2^{n/2}}\frac{1}{(2n!)^{\frac{1}{2}}}\sum_P(-1)^P P\psi_1(1)\psi_2(2)(\alpha_1\beta_2-\beta_1\alpha_2) \times\psi_3(3)\psi_4(4)(\alpha_3\beta_4-\beta_3\alpha_4),\text{ etc.} \quad (1)$$

which expresses the fact that those π electrons which occur on atoms having a double bond between them are paired. Here ψ_{2l} is the wave function of the $2l$th isolated atom, R is the operation of interchanging spins of those electrons that are paired, P is a permutation of the electrons, α, β are the two spin functions, and n is the number of bonds. The structures differ from one another through the different pairings of the electrons.

We then write the wave function for the molecule Ψ as a linear combination of the Ψ^k for each structure, i.e.

$$\Psi=\sum C_k\Psi^k. \quad (2)$$

Ψ must satisfy the Schrodinger equation

$$(H-W)\Psi=0, \quad (3)$$

where the operator

$$H=H^0+\sum_{j=1}^{2n}H_{j,\,j+1} \qquad (2n+1)=1, \quad (4)$$

H^0 is the Hamiltonian of the isolated atoms; $H_{j,\,j+1}$ is the interaction energy between the j and $(j+1)^{st}$ atoms. This means that we consider interaction only between neighboring atoms.

The energy levels are now given by the resulting secular equation

$$\det||(\Psi^j|H-W|\Psi^k)||=0,$$

where

$$(\Psi^j|H-W|\Psi^k)=\int\Psi^j(H-W)\bar{\Psi}^k d\tau. \quad (5)$$

This determinant can easily be factored if one keeps in mind the group of symmetry operations on the molecule.

To set up the determinant we must evaluate the matrix components $(\Psi^j|H-W|\Psi^k)$. This can be done by directly expanding or by expressing the results of this expansion into the following rules:[8]

$$(\Psi^j|H-W|\Psi^k)=U_{jk}(Q-W)+V_{jk}\alpha,$$

$$Q=\int\psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\psi_5(5)\psi_6(6)H \times\bar{\psi}_1(1)\bar{\psi}_2(2)\bar{\psi}_3(3)\bar{\psi}_4(4)\bar{\psi}_5(5)\bar{\psi}_6(6)d\tau,$$

$$\alpha=\int\psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\psi_5(5)\psi_6(6)H \times\bar{\psi}_1(2)\bar{\psi}_2(1)\bar{\psi}_3(3)\bar{\psi}_4(4)\bar{\psi}_5(5)\bar{\psi}_6(6)d\tau,$$

$$U_{jk}=2^{-(n-i_{jk})},$$

$$V_{jk}=2^{-(n-i_{jk})}\sum_\lambda f_\lambda{}^{jk}.$$

i^{jk} and $f_\lambda{}^{jk}$ are obtained from the result of superimposing the bonds of the structure Ψ^j and of Ψ^k; i^{jk} is the number of islands, and the summation λ runs over all pairs of neighboring atoms in the superposition diagram. $f_\lambda{}^{jk}$ turns out to be the following:

[6] A series of papers by Rumer, Teller and Weyl, Gott. Nach. N. P. Klasse 1930, 285; 1931–33; 1932, 337.

[7] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[8] L. Pauling, J. Chem. Phys. **1**, 280 (1933).

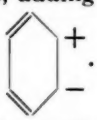
$$f_\lambda{}^{ik}=\begin{cases} 1 \text{ if the atoms have electrons paired.} \\ -\tfrac{1}{2} \text{ if the atoms do not have their electrons paired but are in different islands.} \\ 1 \text{ if the atoms have their electrons unpaired, and are in the same island and an odd number of bonds apart.} \\ -2 \text{ if the atoms have their electrons unpaired, and are in the same island an even number of bonds apart.} \end{cases}$$

In this calculation, as is usually done, we neglect $T^2=(\Psi^i|1|\Psi^j)$ $i\neq j$, compared to 1.

Disregarding T^2 and including only the interactions between neighboring atoms implies the omission of higher order permutations since:

$$(\psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\psi_5(5)\psi_6(6)|H| \times\psi_1(2)\psi_2(1)\psi_3(4)\psi_4(3)\psi_5(5)\psi_6(6)) \sim T^2(\psi_1(1)\psi_2(2)|H|\psi_1(2)\psi_2(1)).$$

Calculation of Wave-Lengths

In the first calculation only singlet nonpolar states of the molecule have been included in the linear combination in formula (2). A further calculation has been made including some ionic terms in the linear combination; that is, adding functions representing structures like  . This latter calculation clears up certain qualitative difficulties, but as yet has not been used for quantitative calculations.

The determinants evaluated for benzene and fulvene omitting the ionic structures are shown in Fig. 6. The canonical set of structures as well as the factored determinant are given.

In the case of azulene, the calculation has been simplified by including in the linear combination only the structures involving one long (i.e., weak) bond. It has been shown[9] that the structures having two long (i.e., of great internuclear distance) bonds do not affect the ground state by more than 1 percent; they would, however, affect the higher levels to a much greater extent. The calculation had to be simplified further since azulene has only two planes of symmetry. The wave functions having long bonds were all given the same coefficient. This approximation has been shown to give the ground state within 2 percent of that found by an amplified calculation.[9]

Giving all the structures with one long bond the same coefficient means that we include in the linear combination (Eq. (2)) one additional function which is completely symmetrical; namely, the sum of all the functions having long bonds. This extra function only affects the energy value of those states which are completely symmetrical, among which is the ground state. To influence the energy value of a state which has a different symmetry, we must include in the linear combination of functions (Eq. (2)) a function which is itself a linear combination of the functions having long bonds and which has the symmetry of the level to be affected.

The lower roots of these determinants are given in Fig. 7.

In order to see whether the splitting up of the energy levels due to this resonance phenomenon is of the correct magnitude we must evaluate α. Instead of making a rough calculation for α, it can be evaluated from thermal data[10] as follows:

$$C_6H_6+3H_2\rightarrow C_6H_{12}+49{,}802\pm150 \text{ cal./mole}$$
$$C_6H_8+2H_2\rightarrow C_6H_{12}+55{,}367\pm100$$
$$C_6H_6+H_2\rightarrow C_6H_8-5565\pm250.$$

Let B equal the hypothetical energy evolved on hydrogenation of a double bond in one structure for a molecule. Now the heat of hydrogenation of benzene to cyclohexadiene, C_6H_8, is smaller than B by an amount equal to the difference between the resonance energies of benzene and cyclohexadiene. Similarly the heat of hydrogenation of benzene to cyclohexane is smaller than $3B$ by the resonance energy of benzene, since cyclohexane has no resonance energy. The ground state of benzene has the energy 2.6α, whereas one Kekule structure which is the structure of lowest energy, has an energy of 1.5α. The difference between the energy of the ground state of the molecule and that of the lowest single structure, 1.1α for benzene, is attributed to resonance. By a similar calculation one finds the resonance energy of cyclohexadiene to be 0.232α. We may then evaluate the heats of hydrogenation of one and of three bonds in benzene, respectively.

$$1.1\alpha+3B=49{,}802, \quad \alpha=-1.92 \text{ volts},$$
$$(1.1-.232)\alpha+B=-5570,^{11}$$
$$B=32{,}872 \text{ cal./mole}.$$

[9] J. Sherman, J. Chem. Phys. **2**, 490 (1934).

[10] G. B. Kistiakowsky, Ruhoff, Smith, and Vaughan, J. A. C. S. **58**, 152 (1936).

[11] This reaction is used instead of $C_6H_{10}+H_2\rightarrow C_6H_{12}$ since the C=C has resonance energy.

Notation $4/6 = 4(Q-W)+6\alpha$

Benzene

A	B	C	D	E		I	II	III	IV	V	
4/6	1/6	2/6	2/6	2/6		5/12	2/6	0	0	0	$A=$
1/6	4/6	2/6	2/6	2/6		2/6	1/2	0	0	0	$B=$
2/6	2/6	4/0	1/6	1/6	=	0	0	1/0	0	0	$C=$
2/6	2/6	1/6	4/0	1/6		0	0	0	1/−2	0	$D=$
2/6	2/6	1/6	1/6	4/0		0	0	0	0	1/−2	$E=$

$I = A+B$
$II = C+D+E$

$III = B-A$
$IV = (D-C)+(E-C)$
$V = (D-C)-(E-C)$

Fulvene

A	B	C	D	E		A	$B+C$	$D+E$	$C-B$	$E-D$
4/6	1/3	1/3	2/6	2/6		2/3	1/3	2/6	0	0
1/3	4/−6	1/3	2/3	2/−3		1/3	5/−3	4/0	0	0
1/3	1/3	4/−6	2/−3	2/3	=	2/6	4/0	5/3	0	0
2/6	2/3	2/−3	4/0	1/3		0	0	0	1/−3	0/2
2/6	2/−3	2/3	1/3	4/0		0	0	0	0/2	1/−1

2/3	1/3	0	0	0
1/3	1/1	0	0	0
0	0	1/−1	0	0
0	0	0	1/−3	0/2
0	0	0	0/2	1/−1

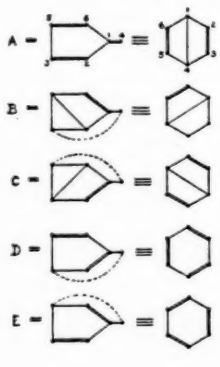


FIG. 6.

The older value[12] of $\alpha = -1.55$ is not used, since in obtaining this value it was assumed that the $>C=C<$ bond has the same energy regardless of the nature of the four groups attached to it, and also the effect of the geometry of the structure upon the strength of binding was neglected. That the former assumption is not justified is seen from the data on heat of hydrogenation of ethylene, heptene[1], pentene[2], etc.[13]

[12] Pauling and Wheland, J. Chem. Phys. **1**, 365 (1933).

[13] Kistiakowsky, Ruhoff, Smith and Vaughn, J. A. C. S. **58**, 144 and 153 (1936).

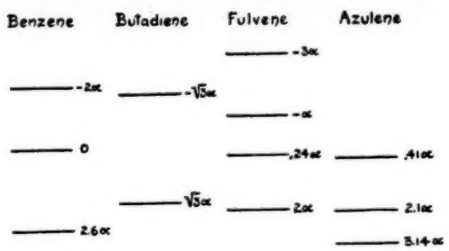
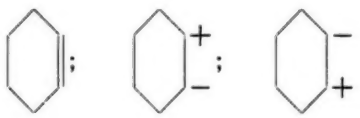


FIG. 7.

More serious is the neglect of the resonance energy of an isolated C=C bond since there may be ionic structures. Furthermore, the -1.55 value is obtained as a small difference between large numbers.

The resonance energy of an isolated carbon-carbon double bond may be evaluated from the following data[13] on cyclohexene, which may resonate between the three structures:



$$H_2+C_6H_{10}\rightarrow C_6H_{12}+28{,}592\pm 100 \text{ cal.}$$

The resonance energy of the double bond is the difference between B and the heat of hydrogenation of cyclohexene.

$$=B-28{,}592=4280 \text{ cal.}=0.19 \text{ volt.}$$

Using $\alpha=-1.92$ we can evaluate the longest wave-lengths from the data of Fig. 7. These are given in Table I together with the experimental values.

The calculation on azulene, the parent substance of a group of naturally occurring substances of physiological interest, is especially illuminating since it is the only hydrocarbon of known structure which is blue. It should be recalled that the values for the wave-lengths given in Table I were calculated without using any spectroscopic values at all. The only experimental data used were heats of hydrogenation.

SELECTION RULES

The symmetry of the wave functions will be discussed with reference to benzene only since its spectrum has been perhaps most thoroughly investigated. The symmetry of the levels may be found from the group theoretical formula[14]

$$a_j=\frac{1}{h}\sum_R \chi(R)\bar{x}^{(j)}(R)=\frac{1}{h}\sum_C h_c\chi(C)\bar{x}^j(C). \quad (6)$$

Here a_j is the number of levels belonging to states which transform like the jth irreducible representation of the group of h symmetry operations, R. The label R runs over operators of the group whereas C runs over the classes of operators; h_c being the number of operators in the class C. $\chi^j(C)$ is the character of the cth class in the jth irreducible representation and $\chi(c)$ is the class character in the reducible representation whose basis is the canonical set of structures. The reducible representation Γ may then be broken into its irreducible parts: $\Gamma=\sum_j a_j\Gamma_j$. The characters of the symmetry operations in the reducible representation, Γ, for benzene are[15]

	E	C_2	C_3	C_6	C_2'	C_2''	i	σ_h	S_6	S_3	σ_v''	σ_v'
Γ	5	3	2	0	1	3	3	5	0	2	3	1

It follows from a comparison with the character table that $\Gamma=2\Gamma_1+\Gamma_{10}+\Gamma_5$. The Γ_5 representation is doubly degenerate as is seen from the character of the identity operation.

The wave functions for the two lowest states are $\Psi_0=\Psi_B+\Psi_A$ and $\Psi_1=\Psi_B-\Psi_A$ respectively (refer Fig. 6). From the table of characters for the group of symmetry operations we can see that Ψ_0 transforms like the first irreducible representation, Γ_1, under the symmetry operations of the group, while Ψ_1 transforms like Γ_{10}. Let us attach a coordinate system to the equilibrium position of each carbon nucleus, placing the z axis perpendicular to the plane of the ring. Now a displace-

TABLE I.

	CALCULATED	OBSERVED
Benzene[a]	2470	2590
Fulvene[b]	3645	3650
Butadiene[c]	1900	2100
Azulene[d]	6914	7000

[a] Cuthbertson and Kistiakowsky, J. Chem. Phys. **4**, 9 (1936).
[b] *Handbuch der Physik*, Vol. 21, p. 105.
[c] Stark and Lipp, Zeits. f. physik. Chemie **86**, 36 (1914).
[d] Plattner and St. Pfau, Helv. Chem. Acta **20**, 225 (1937).

[14] E. Wigner, *Gruppentheorie* (Leipzig, 1931), p. 95.
[15] The notation is the same as that used by E. B. Wilson, Phys. Rev. **45**, 706 (1934). This paper contains the whole character table.

ment in the z direction transforms like Γ_8. The X and Y displacements transform into one another and belong to the degenerate Γ_{12}. The selection rule in its general form may be stated in the following way. "A transition between states transforming like Γ_k and Γ_l respectively is forbidden unless the Kronecker (direct) product $\Gamma_k\Gamma_j\Gamma_l$, where Γ_j is the representation of the electric moment, p, contains the identity representation. Now for benzene

$$p_z^{01} \text{ transforms like } \Gamma_1\Gamma_8\Gamma_{10}=\Gamma_3,$$
$$p_{x,y}^{01} \text{ transforms like } \Gamma_1\Gamma_{12}\Gamma_{10}=\Gamma_5.$$

Since the reduced form does not contain Γ_1 the transition from the ground state of benzene to the first excited state is forbidden. The implications of this result will be discussed later in the paper.

Inclusion of Polar Terms

Great accuracy cannot be expected when the preceding calculation is applied to band groups other than the one at the longest wave-length, since no attempt was made to consider the effect of many highly excited states. Since the high energy states will, no doubt, lower the excited levels more than the ground state, the calculated wave-lengths will be too short. This is indeed found to be so. Fulvene has a second band at 2700A which is calculated to be 2100; the band at 3500 of azulene comes out to be 2400; benzene has a second band at 2000 which is calculated to be 1400. More serious than the inaccuracy in the wave-length is the difficulty that appears in

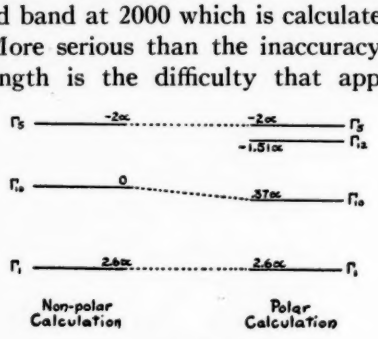
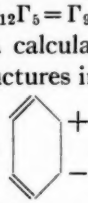
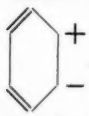


Fig. 8.

intensity considerations. The intensity of the 2000A band in benzene is 1000 times as great as the 2600 band.[18] On the basis of the nonpolar calculation the transition to both the first and second excited states is forbidden. We have seen that the transition from the ground state, Γ_1, to the first excited state, Γ_{10}, is forbidden. The transition to the excited second state, Γ_5 is likewise forbidden, since the third level in benzene has the symmetry Γ_5 and $\Gamma_1\Gamma_8\Gamma_5=\Gamma_{11}$ and $\Gamma_1\Gamma_{12}\Gamma_5=\Gamma_9+\Gamma_{10}+\Gamma_{12}$, neither containing Γ_1.

A calculation was next made including polar structures in the canonical set, that is structures like  . In this calculation two additional constants appear; namely, the coulomb integral for polar states and the resonance integral that occurs in polar nonpolar matrix components.

Twelve polar structures were included in the linear combination for benzene making seventeen structures in all. This is not the total canonical set, as some structures were omitted on energetic grounds in order to keep the determinants small. The twelve structures included are those obtained by rotating and reflecting the structure  . The symmetry of the twelve new states can be found by formula (6) from the characters of the reducible representation on the basis of the twelve structures. The reducible representation Γ is reduced yielding the twelve new states:

$$\Gamma=\Gamma_1+\Gamma_2+2\Gamma_5+\Gamma_9+\Gamma_{10}+2\Gamma_{12}.$$

The new Γ_1 and Γ_{10} levels interact with the nonpolar levels of benzene of the same respective symmetry; it is found, however, that the polar and nonpolar Γ_5 levels do not affect one another. The two new parameters are evaluated from the resonance energy of cyclohexene and from its lowest absorption frequency.[16] A solution of the secular determinant after substituting the values of the parameters yields the following energy levels (Fig. 8). That is, a new polar level of symmetry Γ_{12} appears below the Γ_5 level.

This new level, which is now the third level, has the symmetry Γ_{12} and the transition to it is allowed since $\Gamma_1\times\Gamma_{12}\times\Gamma_{12}=\Gamma_1+\Gamma_2+\Gamma_5$.

The 1000-fold relative intensity is then due to the fact that the 2000A band is not forbidden.

Triplet States

The preceding calculations have included in the linear combination of functions representing the

[16] E. Carr and M. K. Walker, J. Chem. Phys. **4**, 755 (1936). Since the spectrum of cyclohexene was not reported the frequency of pentene-2 was used.

$$\begin{vmatrix} 4/-2, & 1/2, & 0/2, & 1/2, & 0/2, & 1/2, & 2/2, 2/2, 0/2 \\ 1/2, & 4/-2, & 1/2, & 0/2, & 1/2, & 0/2, & 0/2, 2/2, 2/2 \\ 0/2, & 1/2, & 4/-2, & 1/2, & 0/2, & 1/2, & 2/2, 0/2, 2/2 \\ 1/2, & 0/2, & 1/2, & 4/-2, & 1/2, & 0/2, & 2/2, 2/2, 0/2 \\ 0/2, & 1/2, & 0/2, & 1/2, & 4/-2, & 1/2, & 0/2, 2/2, 2/2 \\ 1/2, & 0/2, & 1/2, & 0/2, & 1/2, & 4/-2, & 2/2, 0/2, 2/2 \\ 2/2, & 0/2, & 2/2, & 2/2, & 0/2, & 2/2, & 4/0, 1/2, 1/2 \\ 2/2, & 2/2, & 0/2, & 2/2, & 2/2, & 0/2, & 1/2, 4/0, 1/2 \\ 0/2, & 2/2, & 2/2, & 0/2, & 2/2, & 2/2, & 1/2, 1/2, 4/0 \end{vmatrix} = \begin{vmatrix} 7/8, & 4/6, & 0, & 0, & 0, & 0, & 0, & 0, & 0 \\ 4/6, & 3/2, & 0, & 0, & 0, & 0, & 0, & 0, & 0 \\ 0, & 0, & 1/-4, & 0, & 0, & 0, & 0, & 0, & 0 \\ 0, & 0, & 0, & 1/-1, & 0, & 0, & 0, & 0, & 0 \\ 0, & 0, & 0, & 0, & 1/-1, & 0, & 0, & 0, & 0 \\ 0, & 0, & 0, & 0, & 0, & 2/-2, & 2/0, & 0, & 0 \\ 0, & 0, & 0, & 0, & 0, & 2/0, & 3/-2, & 0, & 0 \\ 0, & 0, & 0, & 0, & 0, & 0, & 0, & 2/-2, & 2/0 \\ 0, & 0, & 0, & 0, & 0, & 0, & 0, & 2/0, & 3/-2 \end{vmatrix}.$$

$2\Gamma_9$ Γ_2 Γ_5 $2\Gamma_{12}$

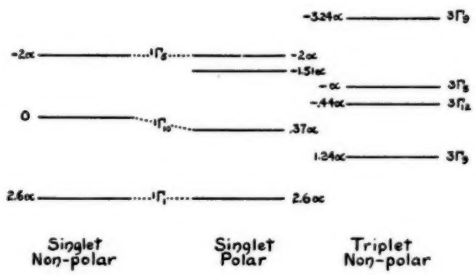
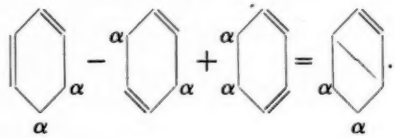


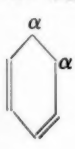
FIG. 9.

state of the molecule only functions in which the molecule has no total spin. There is an entire set of new states, which have a resultant spin of unity, the triplet states. The transition from a singlet to a triplet state is forbidden since the spin functions are orthogonal.

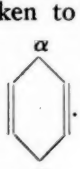
It was supposed that an intercombination band would be very weak in comparison to the other bands. This will be valid for molecules of not too high a symmetry, but may not be valid for benzene since the transition of lowest energy between singlet states is also forbidden, on symmetry grounds. The triplet states of benzene were therefore calculated by the H-L-S-P method. The canonical set is composed of nine structures, as can be seen if one notices that a linear relationship exists between certain structures, namely,



The nine structures forming the canonical set were taken to be the nine orientations of



and



. That there are nine structures can also be seen from formula (7) which gives the number of structures $N(\sigma)$, for each value of σ, the projection of the spin upon an axis; n being the number of nuclei.

$$N(\sigma)=\frac{n!}{((n/2)-\sigma)!((n/2)+\sigma)!}. \qquad (7)$$

The number having a total spin of 1 is $N(1)-N(2)=9$.

The symmetry can be found from formula (6). The characters of the reducible representation on the basis of the nine structures are

	E	C_2	C_3	C_6	C_2'	C_2''	i	σ_h	S_6	S_3	σ_v''	σ_v'
Γ	9	−3	0	0	1	−3	−3	9	0	0	−3	1

so that $\Gamma=\Gamma_2+\Gamma_5+2\Gamma_9+2\Gamma_{12}$.

The secular determinant is given in Fig. 9. Its solution yields the energy levels of the triplet states[17] which are also shown in the figure, the same parameter, α, appearing as it did in the energy of the singlet states.

INTERPRETATION OF BENZENE SPECTRUM

The transitions from the ground state $^1\Gamma_1$ to the $^1\Gamma_{10}$, $^3\Gamma_9$ and $^3\Gamma_{12}$ are all forbidden. The only

[17] The triplet levels obtained by this calculation are in complete agreement with those obtained by Hückel with a more cumbersome method.

allowed transition is to the $^1\Gamma_{12}$ so that we must identify this transition, $^1\Gamma_1 \rightarrow {}^1\Gamma_{12}$ with the 2000A band which is 1000 times as intense as that of 2600. We now have three excited levels remaining and only one observed band, that at 2600A of electron number 10^{-4}. The transition $^1\Gamma_1 \rightarrow {}^3\Gamma_{12}$ has an energy between that of $^1\Gamma_1 \rightarrow {}^1\Gamma_{10}$ and of $^1\Gamma_1 \rightarrow {}^1\Gamma_{12}$ and hence should fall between these

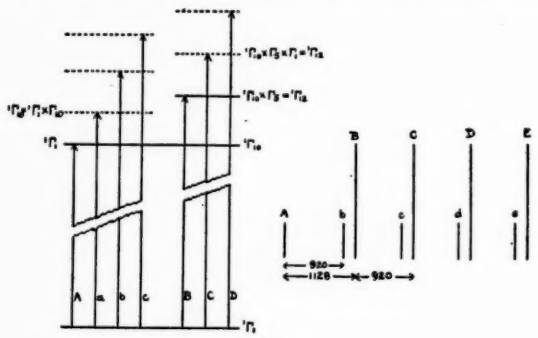


FIG. 10.

bands in the spectrum. Now if the transition $^3\Gamma_2$ is very weak compared to the $^1\Gamma_1 \rightarrow {}^1\Gamma_{10}$ transition, as will be shown to be the case, the former will be marked since it is certainly very weak compared to the allowed transition $^1\Gamma_1 \rightarrow {}^1\Gamma_{12}$ which overlaps the band of the $^1\Gamma_1 \rightarrow {}^1\Gamma_{10}$ transition; the minimum between these two bands (about 150A) is still 20 times as intense as the transition to $^3\Gamma_{12}$ should be. This still leaves the $^1\Gamma_1 \rightarrow {}^3\Gamma_9$ to explain; since this band occurs near the visible, it should be detected. A new band system has now been found by the author at 3400A and will be reported in a later paper. It must be mentioned that in order to observe this 3400 band one needs at least a 20 cm path of liquid benzene, whereas the 2600A band when observed in a 50 cm tube at a pressure of 2 mm shows two progressions clearly, one much weaker than the other. That is, the new band is weaker than the weak progression of the 2600 band by a factor 2×10^{-5}.

We, therefore, identify the 2000A band system as the transition from the ground electronic level to the $^1\Gamma_{12}$ level; the 3400A band is identified with a transition to $^3\Gamma_9$, and the 2600A band is to be correlated with the transition to $^1\Gamma_{10}$. This identification of the band as arising from a transition forbidden on symmetry grounds will be seen to account for the following points in connection with the 2600A band of benzene.

1. The oscillator strength of the band group at 2600A is very weak,[18] being about 10^{-4} electrons.

2. The electric susceptibility of benzene increases with temperature,[19] which contradicts the Langevin-Debye formula.

3. V. Henri[20] has found that the total intensity of absorption of the 2600 band decreases with decreasing temperature.

4. Cuthbertson and Kistiakowsky[21] found two progressions in fluorescence at high pressures, one starting at 38,609 $cm^{-1}=4.77$ volts, and the other starting at 37,481 $cm^{-1}=4.62$ volts. Henri had previously found these two progressions in the absorption of benzene vapor.[22]

5. W. V. Mayneard and E. M. F. Roe[23] find that as one lowers the temperature the extinction coefficient of some band maxima in the 2600A band system increases, whereas that of other band maxima, especially the one at the longest wave-length, decreases as one decreases the temperature.

The transition from the $^1\Gamma_1$ to the $^1\Gamma_{10}$ electronic level may occur in two ways, in spite of the selection rule discussed above. If the molecule is perturbed by other molecules or has its symmetry destroyed by some internal vibration, we can expect a very weak transition in violation of the selection rule.

The molecule may also be excited from the $^1\Gamma_1$ state to certain vibrational levels of the $^1\Gamma_{10}$ electronic state. A transition from $^1\Gamma_1$ to a state of vibrational symmetry Γ_v in the $^1\Gamma_{10}$ electronic state is not forbidden if $\Gamma_1\Gamma_{12}\Gamma_v\Gamma_{10}$ contains Γ_1.

Any transition that is allowed is also allowed in combination with a vibration of symmetry Γ_1. The frequency of the totally symmetrical frequency in benzene is 990 cm^{-1} in the ground state and 920 cm^{-1} in the excited state. Progressions of 920 cm^{-1} spacing should therefore be found in absorption and of 990 cm^{-1} spacing in fluorescence. Now there is in benzene a vibration of symmetry Γ_5 which does make the transition allowed since $\Gamma_1\Gamma_{12}\Gamma_5\Gamma_{10}=\Gamma_1+\Gamma_2+\Gamma_5$.

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[18] N. Chako, J. Chem. Phys. **2**, 644 (1934).
[19] Sanger, Physik. Zeits. **27**, 165 (1926).
[20] V. Henri, Comptes rendus **200**, 1532 (1935).
[21] Cuthbertson and Kistiakowsky, J. Chem. Phys. **4**, 14 (1936).
[22] V. Henri, *Structure des Molecules* (1925), p. 709.
[23] W. V. Mayneard and E. M. F. Roe, Proc. Roy. Soc. **A895**, 647 (1937).

This Γ_5, Raman active, vibrational frequency of 1175 cm^{-1} has been observed in the ground state of benzene. The value of this frequency in the first excited state is not known but will probably be slightly less than 1175 cm^{-1}. It is assumed here that this vibrational frequency in the upper state is 1128 cm^{-1} in order to obtain quantitative agreement with experiments.

The band system in absorption will then appear as two progressions A, b, c, d and B, C, D, E each having its bands spaced 920 cm^{-1}; the two progressions having a relative displacement of 1128 cm^{-1} (Fig. 10). The A, a, b, c band will be weak since it violates the selection rule and can occur only due to perturbations. The perturbations depend upon the temperature since as one cools a crystal down to absolute zero the motions within and between molecules die down. That is, one expects that the extinction coefficient of this progression should decrease with decreasing temperature.

The B, C, D, E progression is also weak since we may write the wave function for electronic and vibrational degrees of freedom.

$$\Psi(e, v)=\psi(e)\psi(v)+\epsilon\psi(e, v).$$

The product $\psi(e)\psi(v)$ gives a zero electric

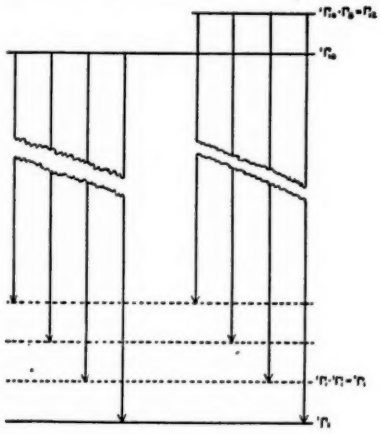

FIG. 11.

moment. The value of ϵ is small, its magnitude depending upon the interaction between vibration and electronic energy. This interaction is affected by temperature only to a second order.

These views are in good agreement with the experiments of Henri and of Mayneard and Roe. Henri finds two progressions in absorption with a relative displacement of 1129 and having a 920 cm^{-1} spacing within each progression. From Fig. 13[23] it is seen that as the temperature is decreased the shoulders of the bands B, C, D, E split into a separate series of peaks, A, a, b, c. Now if the transition probability is independent of the temperature, the peaks should increase in height as

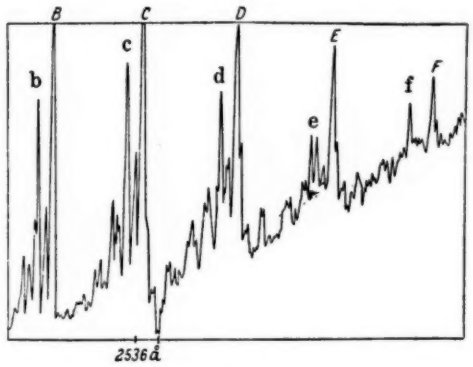

FIG. 12.

the temperature is lowered, first, since a drop in temperature causes a sharpening up of the band; and second, due to the contraction of the absorbing layer which amounts to 15 percent[24] in a fall of 130°. The peaks of the series B, C, D, E do increase greatly as the temperature falls whereas the peaks A, b, c, d, however, decrease, the band A dying out completely at -120°C. The anomalous position of the band A is, of course, evident.

In fluorescence[21] two progressions (excited by the 2536 line of Hg) are also observed, each one being spaced 990 cm^{-1}, the two progressions having a relative displacement of 1128 cm. The 37,481 band is more intense than the 38,609 in fluorescence although it is much weaker in absorption. This relative intensity is independent of the wave-length of the exciting line, as reported by Pringsheim.[25] This can be understood if the vibrational energy in the excited state is lost very quickly so that the fluorescence takes place only from the two levels shown in Fig. 11. That one gets transitions from a molecule vibrating in the upper state at all, is due to the fact that the transition from the Γ_5 vibration in the upper state down to the ground state is not forbidden as are the other vibrations. Its lifetime is therefore much shorter and it may fluoresce before an inelastic collision. Molecules having other vibra-

[24] C. P. Smyth and Stoop, J. C. S. **51**, 3315 (1929).
[25] Pringsheim and Reimann, Zeits. f. Physik **29**, 115 (1924).

tions have a long lifetime and suffer inelastic collisions before radiation and hence can only radiate from the vibrationless excited state.[26] That the 38,609 band system is the weaker of the two in fluorescence, although it is stronger in absorption, is to be attributed to the fact that only few molecules vibrating with a Γ_5 vibration in the excited state will fluoresce before an inelastic collision. Therefore the 38,609 band can be the weaker of the two in spite of the fact that far more molecules are excited to a Γ_5 vibration, as one must conclude from the relative intensity in absorption coupled with the independence of the relative intensity in fluorescence of the exciting line.

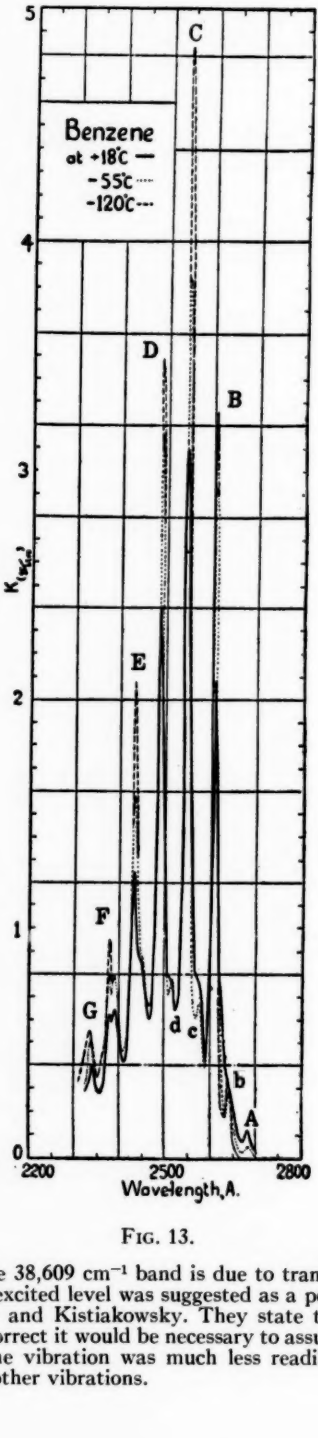

FIG. 13.

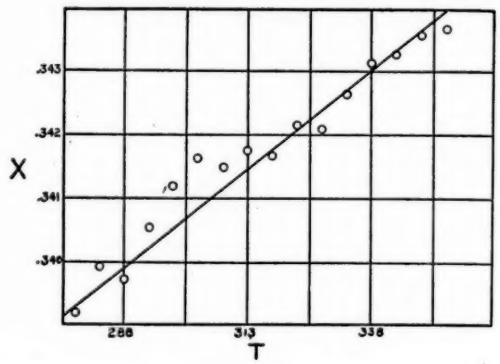

FIG. 14.

The existence of the two progressions is seen in the absorption spectrum of gaseous benzene (Fig. 12).[27] One progression being lettered A, b, c, d, e, (the band A appears outside of this figure but can be seen in Fig. 13), the other B, C, D; each progression having a 920 cm^{-1} spacing. The progressions are also seen in the photometer trace of the liquid (Fig. 13), but in the trace at $(-180°)$ one sees that band A has died out.

The electric susceptibility of benzene (Fig. 14)[19] is seen to increase very slightly with T instead of to decrease as required by the Langevin-Debye formula:

$$\chi=\frac{\epsilon-1}{\epsilon+2}\frac{3}{4\pi}=N\left(\alpha+\frac{\mu^2}{3kT}\right),$$

where

$$\alpha=\frac{2}{3}\sum_{n=1}^{\infty}\frac{|P_{n0}|^2}{h\nu_{0n}},$$

the sum running over all excited states.

The anomaly may be interpreted as due to the fact that α is not a constant but increases with

[26] That the 38,609 cm^{-1} band is due to transitions from a vibrating excited level was suggested as a possibility by Cuthbertson and Kistiakowsky. They state that for this view to be correct it would be necessary to assume that the energy of the vibration was much less readily lost than that of the other vibrations.

[27] A. Kronenberger and P. Pringsheim, Zeits. f. Physik **40**, 83 (1927).

temperature as a result of the increased transition probability of the low frequency transitions at the higher temperatures.

Returning to the levels of benzene shown in Fig. 9 we recall that the entire preceding discussion rests upon and lends weight to the identification of the 2600A bands as a $^1\Gamma_1 \rightarrow {}^1\Gamma_{10}$ transition instead of a transition to $^3\Gamma_{12}$. If this view is correct the transition to $^3\Gamma_{12}$ must be masked by the $^1\Gamma_{10}$ transition and $^1\Gamma_{12}$ transitions as previously discussed. We can estimate the strength of the transition to $^3\Gamma_{12}$ in the following way. The oscillator strength of the $^1\Gamma_1 \rightarrow {}^1\Gamma_{12}$ band is 10^{-1}. The 2600 band, which has a total oscillator strength of 10^{-4}, consists of two progressions, one due to a $^1\Gamma_1 \rightarrow {}^1\Gamma_{10}$ transition, the other arising from a $^1\Gamma_1 \rightarrow {}^1\Gamma_{10} \cdot \Gamma_5$ transition. The former of these bands is 400 times[28] weaker than the latter in the vapor but only 20 times weaker in solution[29] at room temperature. Hence we can say that in solution the $^1\Gamma_1 \rightarrow {}^1\Gamma_{10}$ transition has a strength of 5×10^{-6}. Now the band group at 3400 is 5×10^4 times weaker than the $^1\Gamma_1 \rightarrow {}^1\Gamma_{10}$ transition.[30] Hence the strength of the 3400A band can be estimated to be $\sim 10^{-10}$. Now the 3400 band, although it has not been resolved, should also consist of two progressions, one due to a $^1\Gamma_1 \rightarrow {}^3\Gamma_9$ and the other due to $^1\Gamma_1 \rightarrow {}^3\Gamma_9 \cdot \Gamma_5$. The $^1\Gamma_1 \rightarrow {}^3\Gamma_9$ transition would then have an intensity of 5×10^{-12}. Hence we can say an intercombination causes a decrease in intensity of 5×10^5 whereas a violation of symmetry decreases the intensity by 10^6. The $^1\Gamma_1 \rightarrow {}^3\Gamma_{12}$ should therefore have an intensity of 10^{-7} which would make it 10^3 times weaker than the strong progression of $^1\Gamma_1 \rightarrow {}^1\Gamma_{10}$ and fifty times weaker than the very weak progression. It would therefore be masked, being much weaker than transitions to both the $^1\Gamma_{10} \rightarrow {}^1\Gamma_{12}$ levels. The intensities are summarized in Fig. 15.

It is *a priori* possible that the 2600A band is in reality a $^1\Gamma_1 \rightarrow {}^3\Gamma_{12}$ transition instead of the $^1\Gamma_1 \rightarrow {}^1\Gamma_{10}$ upon which the preceding discussion was based. The great difference in intensity between the two progressions forming this band system speaks against the possibility of a transition to $^3\Gamma_{12}$ since the transition to a Γ_5 vibrational level in the excited state, although allowed, should not be particularly stronger than the $0 \rightarrow 0$ transition which in this case would also be allowed on symmetry grounds. That is, the $^1\Gamma_1 \rightarrow {}^3\Gamma_{12}$ and a $^1\Gamma_1 \rightarrow {}^3\Gamma_{12} \cdot \Gamma_5$ are both forbidden as intercombinations but neither violates symmetry rules. The change in relative intensity from 400 : 1 to 20 : 1 as one goes from the gaseous to the liquid state also favors the $^1\Gamma_{10}$ interpretation, as do also the experiments of W. V. Mayneard and E. M. F. Roe, which show that the relative intensity of the weaker progression compared to the stronger decreases with temperature.

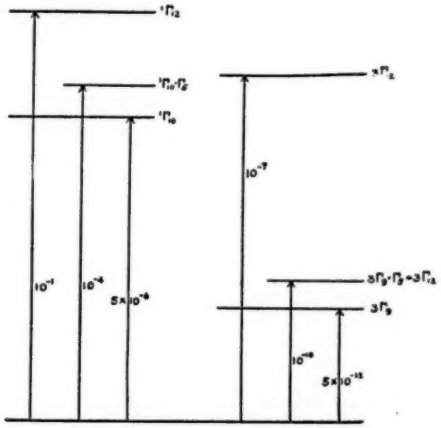

FIG. 15.

I wish to express my sincere thanks to Professor K. F. Herzfeld for suggesting, and together with Dr. M. Goeppert-Mayer, for directing this research.

[28] V. Henri, J. de phys. **3**, 181 (22) Fig. 2. Compare spectra at 0.01 and 3, 4.5, and 5.5 mm pressure.

[29] W. V. Mayneard and E. M. F. Roe, reference .24 Compare bands *A* and *B* at room temperatures.

[30] The weak progression in the 2600 band, i.e., the $^1\Gamma_1 \rightarrow {}^1\Gamma_{10}$ can be observed in a 50 cm tube at 2 mm pressure of benzene whereas one needs at least 20 cm of liquid benzene to see the 3400 band.

Studies in Gaseous Polymerizations

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(Received June 7, 1937)

EARLIER work on simple gaseous polymerizations[1–9] has clearly shown that association reactions of lower dienes follow simple kinetic laws and are amenable to treatment by the newer statistical theories of reaction rates.

The present contribution describes efforts to extend the detailed knowledge of these reactions and also contains a more comprehensive discussion of the reaction mechanism than has been possible with the meager kinetic data heretofore available.

EXPERIMENTAL DETAILS

All observations on the rates of association reactions were made with static systems by following pressure changes and by occasionally analyzing the products. For pressure measurements quartz spiral gauges were employed. In handling compounds with higher boiling points, heated metal valves with Sylphon bellows or heated all-glass valves with silver-chloride-coated seats were used exclusively. Oxygen was kept out of the system by repeated evacuations without intervening admission of air and by careful fractionation of the reactants in vacuum. Unless stated otherwise, no other precautions were employed. Air furnaces, electrically heated and manually controlled, were used except in the work on the association of cyclopentadiene for which an oil bath was employed. Temperatures were read with thermocouples calibrated against a platinum resistance thermometer.

In studying the rate of polymerization of cyclopentadiene in the liquid phase freshly prepared cyclopentadiene, after repeated distillations in vacuum, was condensed in several small tubes which were then sealed off from the evacuating system. They were immersed in a thermostat for varying lengths of time and analyzed by determining their refractive index with a Pulfrich refractometer calibrated beforehand with known mixtures of monomer and dimer. The calibration gave a nearly linear relationship between the refractive index and the weight-concentration of the monomer. In working with solutions of cyclopentadiene in tetrahydronaphthalene, the former was distilled in vacuum into a sample of the solvent which had been previously boiled out in vacuum. The solution was forced by pure nitrogen into several tubes placed in a flask with their open ends, drawn into fine capillaries, pointing downwards. These ends were sealed off after the tubes were taken out of the system. This procedure was necessary because solutions distributed to reaction tubes and sealed off in vacuum became slightly nonuniform due to evaporation of cyclopentadiene and caused inconsistent results. The reaction was followed by withdrawing tubes after various heating periods and observing the refractive indices, this time using a Zeiss portable laboratory liquid interferometer. To calculate the rate constant of the liquid reaction in cc mole^{-1} sec.$^{-1}$, the densities of the various mixtures were determined by the Westphal balance method and found to be additive. It was also found that the vapor pressure of the monomer obeyed Henri's law in dimer and in tetrahydronaphthalene mixtures, showing that these solutions are nearly ideal.

In differentiating between methyl acetylene and allene, the methyl acetylene was absorbed in a potassium iodo mercurate solution[10] contained

[1] Perkin, J. Soc. Chem. Ind. **31**, 616 (1912).
[2] Lebedev, (a) J. Russ. Phys. Chem. Soc. **42**, 949 (1910); (b) ibid. **45**, 1249 (1913); (c) Rev. gén. chim. **18**, 102 (1918); (d) J. Russ. Phys. Chem. Soc. **45**, 1924, 1940 (1913).
[3] Gapon, (a) J. Russ. Phys. Chem. Soc. **62**, 1325, 1395 (1930); (b) ibid. **63**, 496 (1931); (c) Chem. J. Ser. A J. Allg. Chem. **1** (**63**), 765 (1931); (d) J. Gen. Chem. (U.S.S.R.) **1**, 770 (1931).
[4] Staudinger, (a) Trans. Faraday Soc. **32**, 98 (1936); (b) Ber. **46**, 2466 (1913).
[5] Whitby, (a) and Gallay, Can. J. Res. **6**, 280 (1932); (b) and Crozier, ibid. **6**, 203 (1932); (c) and Macullum, Trans. Roy. Soc. Can. **22**, 39 (1928).
[6] Krautz, Nantzov and Sovking, Compt. rend. acad. sci. U.S.S.R. **3**, 265 (1934).
[7] Vaughan, (a) J. Am. Chem. Soc. **54**, 3863 (1932); ibid. **55**, 4109 (1933).
[8] Rice and Gershinowitz, (a) J. Chem. Phys. **2**, 853 (1934); (b) ibid. **3**, 479 (1935).
[9] Kistiakowsky and Lacher, J. Am. Chem. Soc. **58**, 123 (1936).
[10] Hurd and Spence, J. Am. Chem. Soc. **51**, 3354 (1931).

in an analytical shaker[11] and a duplicate device containing 82.4 percent sulfuric acid was used for the allene. In preparing the dimerization product of 1,3-butadiene, a 12-liter reaction vessel was used and the product withdrawn from the flask by evacuation through traps so that the dimer collected was freed of unreacted butadiene.

Compounds

Styrene was obtained from Eastman Kodak Company and was distilled from bulb to bulb in vacuum to free it from polymers and was then distilled into the storage bulb of the apparatus.

Vinyl acetate was part of a sample used for the measurement of its heat of hydrogenation[12] and had been subjected to a careful distillation in a 15-ft. fractionating column.

Chloroprene was kindly presented to us by the duPont Company[13] and was available as a 50 percent solution in naphtha, stabilized by catechol. Bulb to bulb distillations freed it from the solvent and stabilizing agent whereupon it was distilled into the storage bulb and kept in darkness.

Vinyl acetylene was also presented to us by the duPont Company and was in a 50 percent naphtha solution from which it was separated by bulb to bulb distillations.

Allene was part of a sample prepared for heats of hydrogenation measurements[14] and was of a high degree of purity.

Methyl acetylene was prepared by debrominating 1,2-dibrom propane by means of a boiling solution of potassium hydroxide in *n*-butyl alcohol,[15] and was purified by drying and bulb to bulb distillations in vacuum.

Cyclopentadiene was made by cracking pure dicyclopentadiene prepared from crude dicyclopentadiene obtained from Drs. Fraenkel and Landau of Germany. The method has been described elsewhere.[14] Dicyclopentadiene melting from 31.7–32.0° was used to obtain the monomer.

1,3-Pentadiene was part of a sample made for work on its heat of hydrogenation[50] and was of a high degree of purity.

2,3-Dimethyl butadiene-1,3 was also made for the calorimetric work.[50] Unfortunately, sample I, which was a part of the middle fraction from the 15-ft. still, was exhausted before the kinetic measurements were completed. Samples II and III represent fractions collected near the beginning of the distillation and are decidedly inferior, on the basis of their boiling ranges, to sample I. We are unable, however, to estimate the degree of their absolute purity.

1,3-Butadiene was prepared by cracking cyclohexene with a chromel cracking coil.[14] It was purified by bulb to bulb condensation and solidification in vacuum.

Experimental Results

Most of the compounds described in the preceding section showed behavior which made them unsuitable for kinetic studies below atmospheric pressure of the type here intended. Nevertheless, the results obtained will be described briefly, chiefly to spare others unnecessary experimental work.

Styrene is stable to about 400°, but at that temperature a slow reaction begins, accompanied by a decrease in pressure. Apparently, the reaction ceases after a small percentage pressure change. At a slightly higher temperature, 420°, an increase in pressure is observed, indicating the predominance of a decomposition reaction.

Vinyl acetate begins to decompose at about 360° and no temperature range has been found in which a measurable polymerization takes place at pressures below one atmosphere.

Chloroprene begins to polymerize at about 230° but at 260° decomposition becomes predominant. The pressure decreases much less than one would expect even for the formation of a dimer. Thus, at 447 mm initial pressure, the reaction apparently ceases when the pressure drops to about 324 mm. With an initial pressure of 231 mm a drop to only 187 mm is observed.

Methyl acetylene does not polymerize readily even at 475° at which temperature appreciable decomposition occurs. Isomerization to allene is negligible—not exceeding 1 percent which is within the errors of measurement.

[11] Chambers and Kistiakowsky, J. Am. Chem. Soc. **56**, 399 (1934).

[12] See a forthcoming publication from this laboratory for details.

[13] We wish to thank Dr. A. S. Carter of the Jackson Laboratory for this material and also for the sample of vinyl acetylene.

[14] Kistiakowsky, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **58**, 146 (1936).

[15] Tapley and Giesey, J. Am. Pharm. Assn. **15**, 115 (1926).

Allene polymerizes measurably in the temperature range of 320–400°. The kinetics appear to be quite complex; rate constants calculated from point to point increase rapidly with time and

TABLE I. *Vinyl acetylene.*

T °K	533	533	533	577	577	577	613	613	613
P_0 mm	209.1	380.0	443.0	113.1	214.4	602.6	118.4	216.8	361.0
$k_0 \times 10^5$ (% reaction)$^{-1}$ sec.$^{-1}$	0.335	0.512	1.17	0.159	0.257	1.16	0.301	1.24	1.89

TABLE II. *Vinyl acetylene—effect of O_2; 577°K.*

P_0 MM	$k \times 10^5$ (AT 10% REACTION) (% REACTION)$^{-1}$ SEC.$^{-1}$	
186.1	0.386	no oxygen
214.8	0.623	8.9 mm of air

oxygen accelerates the reaction noticeably. No isomerization into methyl acetylene was found to take place. Several workers[2d, 16] have shown that allene and its derivatives can be isomerized into corresponding acetylenes by means of an alkaline catalyst. In pyrolyzing allene and methyl acetylene, Hurd[17] found the polymerization products of both in the pyrolysis of either and concluded that some isomerization was present. The pyrolyses were done between 400–600° with the flow method and a contact time of about one minute. Polymerization and decomposition were the predominant reactions.

The absence of the isomerization reaction is noteworthy as demonstrating that the direct shift of a hydrogen from one carbon atom to another requires a high activation energy, not less than 40,000 cal. if the A factor of its rate constant is of the order of 10^{13}. This observation is probably of quite general validity as suggested by other work in this laboratory on several hydrocarbons.

Vinyl acetylene starts to polymerize appreciably at *ca.* 200°. The reaction was followed between 260–340° with no serious complications from decomposition occurring. However, the pressure drops to one-fourth or even less of the initial pressure, indicating that the reaction does not effectively stop at the dimer stage, as is the case with dienes, but proceeds with undiminished velocity to higher polymers. During a run the order is quite high and so is the dependence on the initial pressure, as shown in Tables I and II. The second order constants in these tables were calculated with percent of the total pressure drop as the measure of the instantaneous concentration of the reactant and extrapolated to initial time. The reaction appears to be reproducible but is accelerated by appreciable quantities of oxygen as indicated in Table II. The disentanglement of the kinetics of the primary reaction from those of the secondary ones would be a rather difficult task and the study of the reaction was abandoned.

In *cyclopentadiene* dimerization the equilibrium is so far on the side of the monomer that pressures near and above one atmosphere must be used to obtain a reasonable extent of the reaction. The decomposition, on the other hand, can be conveniently followed to practical completion at lower pressures. The second order of the association reaction, after correcting for the reverse process, is not well preserved during various runs as will be seen from Table III in which two typical runs have been reproduced. The trend of the constants varies with temperature. The initial constants, however, seem to be decidedly of the second order with respect to the pressure of the reactant, which is encouraging—particularly so because the decomposition reaction is of a good first order during the entire course of different runs as seen in Table IV.

Thus it is believed that drifts of the association rate constants are due to secondary reactions. It will be noted that the addition of a considerable quantity of oxygen does not influence the association reaction, which further lessens the chance for a chain mechanism in this case. Tables V and

[16] Slobodin, (a) J. Gen. Chem. (U.S.S.R.) **4**, 778 (1934); (b) ibid. **5**, 48 (1935).

[17] Hurd and Meinert, J. Am. Chem. Soc. **52**, 4540 (1930).

TABLE III. *Dimerization of cyclopentadiene; gas phase.*

I. 466.6°K P_0 = 1450 mm									
Percent Reactant	96.8	91.2	85.8	80.7	75.0	70.9	67.7	64.4	62.0
k cc mole^{-1} sec.$^{-1}$	10.2	10.5	11.0	12.2	13.3	14.3	15.8	16.9	
II. 426.1°K P_0 = 1380 mm									
Percent Reactant	98.7	96.2	92.5	87.3	82.3	76.3	69.7	64.2	
k cc mole^{-1} sec.$^{-1}$	1.96	2.05	1.83	1.87	1.79	1.77	1.71		

VI give the summaries of the rate constants of the association and decomposition reactions. The former can be cast into the form: $k_{assn} = 8.5 \times 10^7 \exp(-14900/RT)$ cc mole^{-1} sec.$^{-1}$ and the latter: $k_{decomp} = 1.0 \times 10^{13} \exp(-33700/RT)$ sec.$^{-1}$.

The dimerization of pure cyclopentadiene in the liquid phase has been studied by Stobbe and Reuss[18] while quite recently Khambata and Wassermann[19] have briefly reported their results on the rate of dimerization in benzene as a solvent and on the rate of decomposition of the dimer in paraffin oil. Our experiments were performed with pure cyclopentadiene and with cyclopentadiene in tetrahydronaphthalene. In dilute solutions and even in the 50–50 mixture with tetrahydronaphthalene the reaction was found to be of a good second order, but pure cyclopentadiene was found to polymerize in a nearly first-order reaction as noted in an earlier publication,[20] although the initial second-order constants agreed with those obtained in solution.

It was suggested in the preliminary note that this behavior might be of general significance for polymerizations in the condensed phase but in the meantime results have been obtained which definitely show that the anomaly is due to an incorrect estimation of the concentration of

TABLE IV. *Decomposition of dicyclopentadiene; gas phase. 472.4°K.*

P mm	37.6	41.4	45.6	48.5	54.8	58.5	60.9	62.5	64.1
Δt sec.		91	117	95	285	274	292	396	1067
$k \times 10^3$ sec.$^{-1}$		1.60	1.73	1.77	1.82	1.77	1.85	1.60	1.93

TABLE V. *Association of cyclopentadiene; gas phase.*

T °K	P_0 MM	k CC MOLE^{-1} SEC.$^{-1}$	T °K	P_0 MM	k CC MOLE^{-1} SEC.$^{-1}$
393.4	1600	0.467	433.9	1442	2.32
394.6	1052	.438	433.4	1100	2.32
394.6	1880	.448	432.5	1100	2.74
394.6	1835	.493†	432.5	680	2.60
400.2	1217	.505*	451.1	833	4.78‡
413.1	977	1.04	451.1	1240	4.78‡
412.6	1880	1.02	452.1	529	4.65‡
412.1	1066	1.39	452.1	629	4.37‡
411.9	777	1.03	453.1	442	4.93‡
426.1	1380	1.88	453.1	709	4.06‡
432.3	1229	2.48	450.1	526	4.65‡
432.9	373	2.56	463.1	1230	8.07
433.1	896	2.48	465.3	1340	8.37
433.1	678	2.54	466.6	1450	9.56

[18] Stobbe and Reuss, Ann. **391**, 151 (1912).
[19] Khambata and Wassermann, Nature **137**, 496 (1936).
[20] Kistiakowsky and Mears, J. Am. Chem. Soc. **58**, 1060 (1936).

TABLE VI. *Decomposition of dicyclopentadiene; gas phase.*

T °K	P_0 MM	$k \times 10^3$ SEC.$^{-1}$	T °K	P_0 MM	$k \times 10^3$ SEC.$^{-1}$
428.0	157.4	0.060	473.1	16.8	1.57
428.4	155.3	.070	480.1	197.2	3.74
429.6	178.7	.080	483.1	145.1	3.58
455.6	145.1	.53	493.9	19.8	9.24
456.6	60.3	.49	494.0	93.5	9.13
469.1	116.9	1.17*	494.1	31.1	8.54
472.4	37.6	1.75	494.1	83.5	9.32
472.9	106.0	1.93	494.5	32.4	9.52
			495.4	45.4	9.15

* Packed flask.
† Addition of 22 mm air.
‡ These data, because of experimental imperfections, are given less weight than the experiments at 465°.

TABLE VII.

Assn. of Pure Cyclopentadiene 312.7°K				Assn. of Cyclopentadiene in Dimer 344.3°K		
t SEC.	CONC. MOLE/CC	$k \times 10^3$ CC MOLE^{-1} SEC.$^{-1}$	$k^* \times 10^3$ CC MOLE^{-1} SEC.$^{-1}$	t SEC.	CONC. MOLE/CC	$k \times 10^2$ CC MOLE^{-1} SEC.$^{-1}$
0	0.0118			0	0.0027	
3180	.0108	2.63	2.92	1200	.0022	5.94
7200	.0093	3.70	3.55	4740	.0015	6.22
11460	.0083	3.83	2.99	12360	.0010	4.14
26260	.0057	3.92	2.20	16380	.0008	5.29
69240	.0023	5.83	2.82			
				0	.0027	
				20160	.0007	5.20

* Corrected for formation of polymer on the basis of experiments by Terentieff and Solochin[21] and of Stobbe and Reuss.[18]

cyclopentadiene during the latter stages of the reaction. In Table VII are given the results of a run in which pure cyclopentadiene was used as the starting substance and low concentrations of the reactant were obtained by prolonged heating. In the other runs presented the initial substance was a mixture of a small amount of monomer, the rest being dimer, which mixture was made by weighing and was used as reference in interferometer readings. The figures in the table show quite clearly that the dilute mixture gives a good second-order constant instead of following the trend established in the run with pure monomer.

The explanation of this behavior is found in a paper by Terentieff and Solochin[21] who found that a polymer is formed in pure liquid cyclopentadiene in addition to the dimer. According to their data this reaction occurs chiefly in the beginning of the main process and hence the monomer, rather than the dimer, is responsible for the polymer formation. The refractive index of the mixture of monomer, dimer and polymer is

[21] Terentieff and Solochin, Sintet. Kauchuk **5**, 9 (1933).

TABLE VIII. *Dimerization of pure liquid cyclopentadiene. Rate constants from extrapolation to zero time.*

T °K	k_0 cc mole^{-1} sec.$^{-1}$
273.1	4.50×10^{-5}
313.0	2.82×10^{-3}
317.9	3.50×10^{-3}
331.3	1.30×10^{-2}
333.1	1.05×10^{-2}
353.1	4.63×10^{-2}
354.1	4.50×10^{-2}
354.3	6.00×10^{-2}
344.3	5.26×10^{-2} (in dimer solution)
344.3	2.80×10^{-2} (interpolated for pure monomer)
344.3	4.14×10^{-2} (tetrahydronaphthalene solutions)

TABLE IX. *Association of cyclopentadiene in tetrahydronaphthalene.*

T °K	Conc. mole/cc	k cc mole^{-1} sec.$^{-1}$
344.3	0.39×10^{-3}	4.82×10^{-2}
344.3	1.28	3.99
344.3	1.28	4.18
318.1	6.44	0.538
318.1	6.44	.516
318.1	1.40	.556

different from a mixture containing only the dimer and the same amount of monomer, such as those used for the calibration of the refractometer[22] and hence an error is committed in following the course of the reaction by the refractometer. The percentage error in determining the concentration of the monomer increases rapidly towards the end of the reaction, the amount found being smaller than that actually present. Hence the rising second-order constants. Of course, because of the method of preparation, the correct concentration of the monomer was known in those runs in which prepared monomer-dimer mixtures were used by us and hence these runs gave results agreeing essentially with the initial constants of the others. The second-order constants of the pure monomer runs were extrapolated to initial time (see Table VIII) and the resulting k_0's, when plotted logarithmically against inverse temperature, gave a reasonably straight line. The rate constant is found to be: $k=2.0\times10^9 \exp(-17100/RT)$ cc mole^{-1} sec.$^{-1}$.

Table IX gives the results of polymerization runs in tetrahydronaphthalene as solvent. It was unnecessary to extrapolate to initial time because the second order held quite well in these runs, except in the 50 wt. percent mixtures which showed a slight rise in their second-order constants—doubtless attributable to the occurrence of a slight polymerization to high molecular weight compounds.

Taking the averages of the rate constants at the two temperatures and evaluating from them the activation energy, the rate constant is cast into the form: $k=4.2\times10^9 \exp(-17300/RT)$ cc mole^{-1} sec.$^{-1}$. This expression agrees, as well as can be expected, with the data obtained with solutions of monomer in dimer. There is, however, a larger discrepancy with the results in pure monomer, as will be seen by inspecting the bottom of Table VIII. It is believed that the latter data are at fault because only at lower temperatures was the correction by the method of Terentieff and Solochin successful in producing a second order rate. At higher temperatures, even after correction, the second order constants showed a tendency to increase during a run. One must conclude that here the polymerization is more pronounced (compare data on gas phase association for similar tendencies) and that altogether the extrapolation to initial time gives only the order of magnitude of the rate constant.

The results of the present studies on liquid phase polymerization agree with other available data. Thus, Stobbe and Reuss[18] got for 20°: $k=3.3\times10^{-4}$ cc mole^{-1} sec.$^{-1}$ (as calculated by us) whereas the previously given expression yields for 20°: $k=3.1\times10^{-4}$ cc mole^{-1} sec.$^{-1}$. Khambata and Wassermann[19] select for their data in benzene solution the representation: $k=1.2\times10^9 \exp(-16400/RT)$ cc mole^{-1} sec.$^{-1}$; for 71°C this gives: $k=4.6\times10^{-2}$ and we find for tetrahydronaphthalene solution: $k=4.3\times10^{-2}$. Notwithstanding considerable difference in the

TABLE X.

Δt sec.	1,3-Pentadiene P, mm	652.9°K k cc mole^{-1} sec.$^{-1}$
0	315.0	
285	294.0	70.4
180	283.7	67.5
235	273.1	63.0
245	264.1	60.6
390	252.7	58.6
380	244.1	55.8
630	233.6	51.7
1315	220.9	40.2

[22] Dimer was freshly distilled to free it from polymer for this purpose.

form of the expression, gas phase data also lead to nearly the same rates. By extrapolation to 71°, $k=3.1\times10^{-2}$ cc mole^{-1} sec.$^{-1}$. The present data on the dissociation of dicyclopentadiene in the gas phase and those of Khambata and Wassermann on the reaction in paraffin oil, $k=6\times10^{12}$ exp $(-34000/RT)$ sec.$^{-1}$, while superficially similar, give quite different rates; thus at 500°K the gas rate is 2.5 times faster, so that in the liquid the equilibrium is shifted to the side of the dimer.

TABLE XI.

2,3-DIMETHYL BUTADIENE-1,3 Δt SEC.	P, MM	652.6°K k CC MOLE^{-1} SEC.$^{-1}$
0	194.8	
180	191.1	46.0
540	181.6	45.6
180	178.8	46.0
600	170.7	46.0
600	165.2	37.8
300	163.4	27.2
660	160.8	19.1
540	159.8	9.4

1,3-Pentadiene and 2,3-dimethyl butadiene-1,3 polymerize to dimers at measurable rates not unduly complicated by side rdactions. Tables X and XI show the order of reaction during typical runs, while Tables XII and XIII are summaries of all the constants obtained.

The second order is seen to be reasonably well preserved during the initial stages of the reactions. At later times the constants fall off. The explanation of this behavior is to be found in decomposition (either of the reactants or the reaction products) accompanied by an increase in pressure, in complete analogy with the observations of Vaughan[7b] on isoprene. The side reactions are relatively more pronounced at higher temperatures. Thus, in the case of 1,3-pentadiene, at 279° an initial pressure of 265 mm decreased to 162 mm (61 percent of the initial) but at 380° the pressure decrease was from 315 mm to 214 mm (68 percent). With 2,3-dimethyl butadiene-1,3 at 307.5°, the final pressure was 64.2 percent of the initial (290 mm to 186 mm) while at 352° the pressure dropped from 264 mm to only 206 mm (78 percent).

In addition to the decomposition, some formation of higher polymers also goes on, as evidenced by the presence of practically nonvolatile products. Thus, the interpretation of the latter stages of the reaction is rather uncertain and even in the beginning one is not justified in ascribing the entire pressure change to the formation of the dimers. However, because of the difficulty of more exact identification of the course of these reactions, it has been assumed here that in the beginning the entire pressure change is due to the dimer formation. It is to be noted that Vaughan[7a] found with 1,3-butadiene that the second order constants increased during his runs. Hence, the decomposition is less important in this case than the formation of polymers, which is contrary to what has been observed for the other dienes.

With 2,3-dimethyl butadiene-1,3[23] an additional difficulty was encountered in that the three samples tried gave discordant results. The rates obtained with sample I were 17 percent and 43 percent faster than those found with samples II and III, respectively. However, the temperature coefficients are identical within experimental errors. Furthermore, each sample gave self-consistent results and the rates appeared to be uninfluenced by traces of oxygen. In view of this we are inclined to interpret the discrepancy as being due to a greater purity of sample I. If

TABLE XII. *1,3-Pentadiene.*

°K	k CC MOLE^{-1} SEC.$^{-1}$	°K	k CC MOLE^{-1} SEC.$^{-1}$
552.1	1.85	652.9	67.8
552.1	1.86	652.9	66.8
616.6	22.4	652.9	64.7
616.6	22.5	668.9	109.3
651.8	68.3	692.1	221.0

TABLE XIII. *2,3-Dimethyl butadiene-1,3.*

SAMPLE I		SAMPLE II		SAMPLE III	
°K	k cc mole^{-1} sec.$^{-1}$	°K	k cc mole^{-1} sec.$^{-1}$	°K	k cc mole^{-1} sec.$^{-1}$
582.1	4.4	626.8	18.3	610.6	10.0
652.6	46.0	626.8	18.3	611.4	9.5
653.6	50.8	653.1	39.4	655.5	33.8
653.6	44.6	654.3	43.0	655.8	36.0
654.1	49.9	668.6	59.1	655.8	35.7
668.6	69.1	668.6	69.3	670.3	54.8
673.1	96.7	672.1	70.1	670.3	57.6
				670.3	53.9
				671.1	53.5

[23] Samples of 2,3-dimethyl butadiene-1,3 that were sealed in absence of air and kept indefinitely at room temperatures polymerized into solid, white masses.

sample I is assumed to be 100 percent pure, sample II must contain *ca.* 8 percent and sample III *ca.* 17 percent of nonpolymerizable impurities. It is to be noted in this connection that Kistiakowsky and Lacher[9] reported slightly higher rates with 1,3-butadiene and isoprene than those given by Vaughan.[7] Since the latter used compounds of an ordinary degree of purity, as contrasted with highly purified samples of the former, it was also concluded that impurities accounted for the discordant results. In view of the difficulty of purifying these compounds, such an explanation seems to us to be entirely reasonable, but the A factors of all the rate constants must be regarded as uncertain perhaps to the extent of 20 percent. Since the uncertainty arising from errors in the determination of the activation energies is many times greater, this added error is not very serious.

The activation energy of the 2,3-dimethyl butadiene-1,3 polymerization is found to be 25,300 cal.; $k=1.45\times10^{10}\exp(-25300/RT)$ cc mole^{-1} sec.$^{-1}$.

A similar plot of the data from Table XII leads to an activation energy of 26,000 cal. for 1,3-pentadiene and $k=3.5\times10^{10}\exp(-26000/RT)$ cc mole^{-1} sec.$^{-1}$.

The literature contains several reports on the structure of the dimers formed in polymerization of the dienes. Lebedev[2] identified the product of the dimerization of 1,3-butadiene as 1-vinyl cyclohexene-3 and later studies by many workers[2, 3, 24–31] showed that the homologs of 1,3-butadiene also underwent simultaneous 1,4- and 1,2-addition, thereby making this reaction completely analogous to the Diels-Alder condensation.[32–35] The compounds analyzed were obtained by heating sealed tubes filled with dienes and hence were formed at high pressures of the vapor or even in liquid phase reactions. Vaughan[7a] reported, on the other hand, a dicyclic compound as the dimerization product of 1,3-butadiene at higher temperatures and low pressures. However, his very small samples were collected at the ends of runs and were allowed to stand exposed to air for varying lengths of time. It seemed advisable, therefore, to redetermine the structure of this dimer. 1,3-Butadiene vapor was heated at pressures below atmospheric and at temperatures close to 370° in a 12-liter flask for sufficient lengths of time to produce *ca.* 50 percent conversion according to the data of Vaughan. Combined products from several runs were subjected to fractionation in a three-foot Podbielniak-type column. The main fraction (but by no means all—considerable quantities of higher boiling material remained in the pot) boiled at 129.4±0.5° at 760 mm; refractive index, $n^{20}D=1.4637$; density = 0.8237 at 25°. The molecular refraction, therefore, is 36.16 whereas the theoretical molecular refraction[36] for the product of 1,4- and 1,2-addition is 36.22. A portion of the dimerization product was hydrogenated by the Adams catalyst at room temperature without a solvent.[37] The sample took up 1.68 mole of hydrogen per mole of sample and the physical constants of the product were: b.p. 131.2° at 760 mm; $n^{20}D=1.4333$ and $d_{25°}=0.7811$, which constants agree closely with those of ethyl cyclohexane. Another portion of the product was brominated at −5° and twice recrystallized from alcohol. M.p. = 69–71° which agrees with the melting point of 3,4,1^1,1^2-tetrabrom-1-ethyl cyclohexane. In view of all these data, no doubts can remain that in the high temperature, low pressure reaction the addition goes via the same chemical mechanism as the dimerization at lower temperatures and high concentrations.[38] Similar tests were not performed on other open chain dienes herein investigated but little doubt can exist that their products are also cyclohexene derivatives.

[24] Richard, Comptes rendus **153**, 116 (1911).
[25] Kogerman, Naturforscher Ges. **41**, Nr. 3/4, 59 (1934).
[26] Slobodin, J. Gen. Chem. (U.S.S.R.) **5**, 1415 (1935).
[27] Harries, Ann. **383**, 157 (1911).
[28] Aschan and Krohen, (a) Ber. **57B**, 1959 (1924); (b) Ann. **439**, 221 (1924).
[29] Tilden, J. Chem. Soc. **45**, 410 (1884).
[30] Wallach, Ann. **227**, 295 (1885); J. Chem. Soc. **48**, 550 (1885).
[31] Ostromislensky and Koschelev, J. Russ. Phys. Chem. Soc. **47**, 1928 (1915); J. Soc. Chem. Ind. **35**, 368 (1916).
[32] Diels and Alder, (a) Ann. **460**, 119 (1928); (b) ibid. **470**, 68 (1929).
[33] Alder, *Handbuch der biologischen Arbeitsmethoden*, ed. Abderhalden, Teil 2, 2 Hälfte, Heft 9 (1933).
[34] Kohler and Kable, J. Am. Chem. Soc. **57**, 917 (1935).
[35] Littmann, ibid. **58**, 1316 (1936).

[36] Getman and Daniels, *Outlines of Theoretical Chemistry*, fifth edition (J. Wiley and Sons, Inc., New York, 1931), p. 93.
[37] The low pressure hydrogenation outfit and the catalyst were the property of Dr. E. B. Hershberg of this laboratory who kindly placed them at our disposal.
[38] Cf. also Woljinski, Jegis, Rubin and Shereuretieff, Sintet. Kauchuk **5**, 8 (1936), who arrive at the same conclusion.

TABLE XIV.

ASSOCIATIONS	RATE CONSTANT CC MOLE^{-1} SEC.$^{-1}$	REF.
2 1,3-Butadiene	$4.7 \times 10^{10} \exp(-25300/RT)$	7a
2 Isoprene	$5.3 \times 10^{11} \exp(-28900/RT)$	7b
	$(4.7 \times 10^{10} \exp(-25900/RT))$	
2 1,3-Pentadiene	$3.5 \times 10^{10} \exp(-26000/RT)$	
2 2,3-Dimethyl butadiene-1,3	$1.45 \times 10^{10} \exp(-25300/RT)$	
2 Cyclopentadiene	$8.5 \times 10^{7} \exp(-14900/RT)$	
1,3-Butadiene and acrolein	$1.46 \times 10^{9} \exp(-19700/RT)$	9
Isoprene and acrolein	$1.02 \times 10^{9} \exp(-18700/RT)$	9
1,3-Butadiene and crotonic aldehyde	$0.90 \times 10^{9} \exp(-22000/RT)$	9
Cyclopentadiene and acrolein	$1.02 \times 10^{9} \exp(-15200/RT)$	9
Decompositions		
Endomethylene-2,5-tetrahydrobenzaldehyde	$2.2 \times 10^{12} \exp(-33600/RT)$ sec.$^{-1}$	9
Dicyclopentadiene	$1.0 \times 10^{13} \exp(-33700/RT)$ sec.$^{-1}$	

The product of the dimerization of cyclopentadiene has been discussed in the literature and its structure identified as that resulting from 1,4- and 1,2-addition. According to Alder and Stein,[39] the dimer exists in two forms, α and β, which can be respectively described as the "chair" and the "trough" of the tricyclic compound. The second predominates at temperatures below 170° and it is reasonable to think that in the present research this form was the main product, although some divergence between the results of the gas phase experiments, performed at higher average temperatures, and those in the liquid phase can be tentatively ascribed to the formation of the two different forms.

INTERPRETATION OF THE RESULTS

Results obtained in this and in earlier work on the rates of 1,4- and 1,2-addition reactions of the dienes are now sufficiently numerous to permit an attempt at a more comprehensive treatment of their kinetics. In Table XIV all the pertinent data have been summarized. The association reactions can be divided into three main groups according to the magnitude of their temperature-independent factors. The four 1,3-butadiene polymerizations have, within experimental error, identical A factors. Isoprene constitutes the only appreciable deviation but this reaction according to Vaughan is not very clean. Furthermore, its activation energy falls entirely out of line with those of its homologs, both the less and the more complex ones. When the absolute rates are computed, isoprene is found to have a rate falling between those of 1,3-butadiene and 1,3-pentadiene.[40] Hence the abnormality of the A factor of isoprene may be attributed to experimental imperfections and the rate expression considered to be approximately that given in brackets. It is, however, rather difficult to believe that the temperature independent constants of all these four reactions should be reduced by a further average factor of thirty—or those of the four Diels-Alder condensations increased by the same factor—to make the constants of all eight reactions identical. A careful study of all plausible systematic errors fails to reveal any justification for such a change[41] and we must consider, provisionally at least, the A factors in the two groups as being distinctly different. Also, the polymerization of cyclopentadiene can hardly be brought into agreement with the others. In order to do so one must alter rate constants at the extreme ends of the temperature range covered by nearly 50 percent.[42] If the gaseous rate ex-

[39] Alder and Stein, Ann. **504**, 219 (1933).

[40] Thus, at 350° the rate constants of these four reactions, in their order as in Table XIV, are: 63, 38, 26 and 19.5 cc mole^{-1} sec.$^{-1}$. It is to be noted that the variations are quite small and in no way confirm the statement of Gapon (reference 3b) that the introduction of each methyl group into 1,3-butadiene decreases the rate by a factor of six.

[41] Particularly convincing evidence against systematic errors is that the drifts of rate constants during the course of a run in these eight reactions are in no way correlated to the magnitude of their A factors.

[42] The A factors of the other reactions are on the whole more reliably determined but individual variations of almost a factor of ten are not excluded. Quite recently Khambata and Wassermann, in a short note (Nature **139**, 669 (1937)), report the gaseous association rate of cyclopentadiene to be given by $1.3 \times 10^{9} \exp(-16700/RT)$ cc mole^{-1} sec.$^{-1}$. The temperature range covered in their experiments is smaller than ours. Since this expression agrees more closely with that of the liquid phase reaction, it is inherently more probable. The difference may well be within the combined experimental errors and in the absence of more detailed information it is impossible for us to evaluate critically the relative merits of the two sets of experiments.

pression is correct, the change of the A factor of this association reaction in going from the gas phase to solutions forms an interesting example of the effect of liquid state of aggregation on the form of rate expressions.

Both decompositions are fairly clean-cut reactions and on this score no particular objections to the rate data can be raised. However, the temperature ranges covered are small and particularly in the case of endomethylene-2,5-tetrahydrobenzaldehyde a considerable error in the activation energy is not excluded since the instantaneous concentrations of the reactant could only be estimated from the total pressure changes in the reaction and were quite low in practically all of the experiments.

In an earlier paper Kistiakowsky and Lacher[9] have discussed the statistical calculation of the temperature independent factor assuming that the intermediate complex has a structure very similar to that of the final addition product. Their conclusion was that, while the agreement was not too good, the statistical treatment on this basis did give reasonable results. The real situation, however, is more involved than they have inferred. Since the A factor of the decomposition reaction of endomethylene-2,5-tetrahydrobenzaldehyde has a magnitude of slightly less than kT/h, the activated complex cannot be more loosely bound together than the associated molecule. Therefore, this latter, just as the activated complex itself, must contain six frequencies of a magnitude of 100–150 cm^{-1} and these do not include torsional and other vibrations of the side chains because in the treatment of association reactions to the first approximation they cancel against the corresponding vibrations of the monomer reactant molecules. The situation is still less satisfactory for the associations of 1,3-butadiene and its homologs, as even lower frequencies must be assumed for the ring because of their larger A factors. While no complete analysis of the vibrational frequencies of cyclohexene is available, the existent data[43] strongly discourage this assumption.

Thermodynamic considerations also show that something must be wrong with the data; namely, the entropy change in the Diels-Alder condensation of acrolein and cyclopentadiene, as calculated from kinetic data, is impossibly small: 37 E.U. (at 1 atmos.). It is of the order of magnitude of the entropy change in additions of halogen hydrides to isobutene[44] and is actually a little smaller than the entropy change in typical polymerizations of two mono-olefins to another mono-olefin such as the condensation of two molecules of propylene to one of n-hexylene.[45] In the former of these reactions one of the reactants is a diatomic molecule and in both processes the reaction does not lead to a stiffening of the molecular structure as it does in diene polymerizations. Hence, a much greater entropy decrease is to be expected for this latter type of reaction. The newly added cyclopentadiene polymerization does show the expected entropy change (50 E.U.) and a simple comparison with this reaction would suggest that the error lies in the A factors of the other eight association reactions. However, this seems to us most unlikely. The reactions have been studied by three investigators, using independently calibrated temperature and pressure measuring devices and techniques which were different in many details. We are confident that the error must lie with the rate constant of the only known decomposition reaction of this group—that of endomethylene-2,5-tetrahydrobenzaldehyde. Instead of the measured value of 2×10^{12} $sec.^{-1}$, the A factor for this reaction must be of the order of 10^{15} which would bring the entropy change for this reaction into line with those of others.

The numerically large A factors of both forward and reverse rates of the association reactions are to be interpreted statistically as meaning, in the terminology of Eyring,[46] that the activated complex has a very loose structure. This requirement is met if the activated complex is supposed to have essentially the configuration of a free radical. But other evidence, to be considered presently, suggests that free radicals may have a more real existance than that of activated complexes and hence the detailed reaction mechanism should involve the association of two molecules,

[43] Kohlrausch, *Der Smekal-Raman Effekt* (J. Springer, Berlin, 1931).

[44] Kistiakowsky and Stauffer, J. Am. Chem. Soc. **59**, 165 (1937).

[45] Parks and Huffman, *Free Energy Changes of Organic Compounds* (Chemical Catalog Co., New York, 1932), p. 81.

[46] Eyring, J. Chem. Phys. **3**, 107 (1935).

via an activated complex, to a free radical, which then may, through another active configuration, form the ring structure characteristic of the final product. The concept of free radical intermediates in polymerizations of unsaturated compounds is not new but to conserve space the pertinent literature will not be reviewed. The free radical in the case of 1,3-butadiene must have the structure:

I. $C=C-\dot{C}-C-C-\dot{C}-C=C$

or, in the simplest Diels-Alder condensation:

II. $C=C-\dot{C}-C-C-\dot{C}-C=0.$

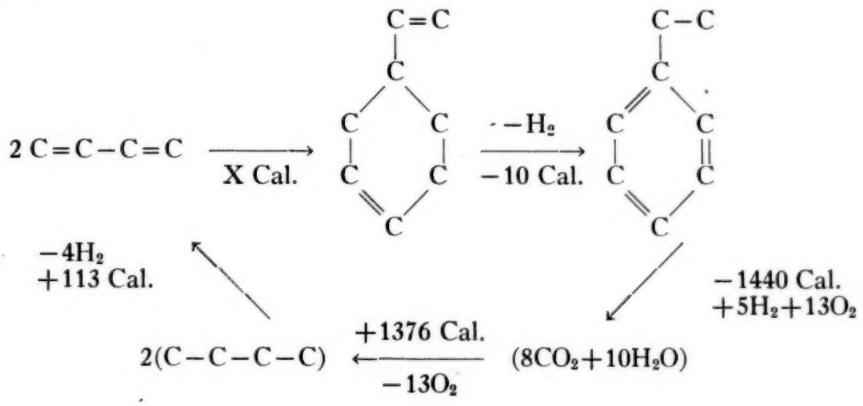
The first question is whether enough energy is available to form such radicals. With activation energies of the order of only 15,000–25,000 cal. it might seem most unlikely, but it should be remembered that radicals of this type can be stabilized by resonance. It is readily seen that four energetically equivalent electronic structures are possible for both molecules I and II:

I(*b*) $C=C-\dot{C}-C-C-C=C-\dot{C}$;

I(*c*) $\dot{C}-C=C-C-C-\dot{C}-C=C$;

I(*d*) $\dot{C}-C=C-C-C-C=C-\dot{C}$

Dr. J. B. Howard of this laboratory has kindly calculated for us by the method of Pauling[47] the magnitude of this resonance energy using for the unknown exchange integral the value deduced by Pauling from his interpretation of benzene resonance. The energy which Dr. Howard finds, 1.4 ev (32.2 Cal.), is undoubtedly too large as are practically all of the resonance energies thus calculated. If it is multiplied by a factor of 0.5, which brings calculation and experiment into fair agreement in many other cases,[14] a value of some 15–20 Cal. results which may be regarded as substantially correct. Together with the activation energy of the association reactions, there are thus some 35–50 Cal. available to form the radical. To connect this figure with the more familiar thermochemical data, consider the following cycle:



in which all steps, except the heat of combustion of ethyl benzene,[48] have been taken from Rossini's data[49] or calculated from the heats of hydrogenation[14, 50] so that the result, $X = -39$ Cal., is fairly reliable.

The reaction in which 39 Cal. are given off involves the breaking of two double bonds to single ones and the formation of two single bonds. Hence, the difference of energy requirements of the processes: $C=C \rightarrow \dot{C}-\dot{C}$ and $C-C \rightarrow \dot{C}+\dot{C}$ is 19.5 Cal. or, correcting for *ca.* 3 Cal. resonance energy in 1,3-butadiene, is approximately 22.5 Cal.[51] The process of formation of the intermediate free radical involves the breaking of two

[47] Pauling and Sherman, J. Chem. Phys. **1**, 362, 606, 679 (1933).
[48] Kharasch, Nat. Bur. Stand. J. Research **2**, 359 (1929).
[49] Rossini, ibid. **12**, 735 (1934).
[50] Dolliver, Gresham, Kistiakowsky and Vaughan, J. Am. Chem. Soc. **59**, 831 (1937).

[51] Compare this value with 20.5 cal. for the difference in heats of reaction between *n*-hexylene plus hydrogen to give *n*-hexane and *n*-hexane plus hydrogen to give two molecules of propane (reference 48).

double bonds (to single ones) and the formation of a new single bond. To allow this reaction, the following condition must be satisfied:

> Energy of opening two double bonds to two single bonds + resonance in two 1,3-butadienes —energy of breaking a single bond—resonance in the radical <25 Cal., the activation energy.

Combining this with the above figure, we find that, for free radicals to be formed, the energy of the single carbon-carbon bond must be not greater than 78 Cal., while the energy of opening a double bond must not be greater than 56 Cal. These figures are of a sensible magnitude, similar to those suggested in many recent publications on the kinetics of organic reactions; they cannot be materially raised without sacrificing the kinetic explanation of the decompositions of organic iodides by the catalysis of iodine atoms for which abundant evidence is available.[52] The conclusion is that the thermal data now available do not exclude the formation of the free radicals.

There is considerable evidence, into the discussion of which we will not enter because of space considerations, that the dimer with the ring structure once formed does not undergo further polymerization. To account for the formation of open-chain polymers in conjunction with the dimer,[53] one must therefore suppose that two quite independent reactions occur simultaneously which have nearly identical activation energies,[2d] because dimers and polymers are formed in commensurate yields over very wide temperature ranges in a given reaction. This is quite unnecessary if the free radicals are supposed to be formed and to have a life long enough that they may undergo further addition reactions—perhaps involving small activation energies. This process will preponderate under conditions of high concentration, whereas at low pressures of the gases the main reaction is the rearrangement of the radical into the stable six-membered ring structure. If the primary reaction is the same for the formation of both the polymer and the dimer, the increase in the amount of the former with increasing concentration of the reactants must occur at the expense of the latter, whereas if the two reactions are independent, such a relation should not be found. This seems to be suitable for an experimental test and experiments in this direction are now in progress in this laboratory.

The observation of Diels and Alder[32a] that transient color accompanies rapid diene synthesis, which has been quoted by Littmann[35] in support of the radical theory, is undoubtedly favorable, but so far color has been observed only in reactions involving quite complex molecules and other explanations are possible.

The intermediary free radical may also be used to explain the action of oxygen in accelerating polymerization at low temperatures by supposing that the oxygen is attached to one of the free valencies in a peroxide-like structure thereby preventing closure of the ring and encouraging further polymerization. This may occur in the instant of the primary reaction, making its activation energy and A factor quite different from those here described, or follow it after formation of the dimer radical. That the oxygen has no effect on these association reactions at high temperatures (see Vaughan, reference 7a) should be interpreted as meaning that now the peroxide has become too unstable to determine the kinetic course of the reaction.[54]

We now turn to kinetic data which may be adduced to support the radical mechanism. A comparison of the activation energies of the nine association reactions involved is not decisive, but the evidence offered by the A factors is much more convincing. It has been pointed out before that the assumption of ring structure for the activated complex leads to impossibly low frequencies of the dimer molecule. If the activated complex has the structure of a free radical, this difficulty disappears because now some of the

[52] Ogg, Trans. Faraday Soc. **31**, 482, 1385 (1935); J. Am. Chem. Soc. **56**, 526 (1934); ibid. **58**, 607 (1936). In the last paper Ogg interprets the mechanism of the decomposition of ethylene diiodide, studied by Arnold and Kistiakowsky, J. Chem. Phys. **1**, 166 (1933), in a way which suggests that the opening of a double bond requires only 25 Cal. This leads to highly improbable consequences and we must decline his interpretation of the reaction and retain instead the mechanism developed originally by Arnold and Kistiakowsky.

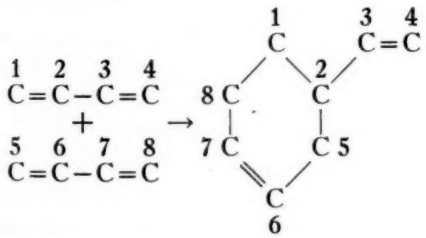
[53] Littmann (reference 35) has recently shown that, when polymers are formed in the Diels-Alder reaction in very concentrated mixtures, they contain both reactants in the molecule rather than the diene hydrocarbon alone.

[54] A situation analogous to this exists in the chlorine-carbon monoxide reaction where inhibition by oxygen, presumably due to the formation of ClO_2, ceases at higher temperatures because of the greater instability of this compound.

newly formed internal degrees of freedom are either free rotations or very slow torsional oscillations of an open chain around carbon-carbon single bonds.

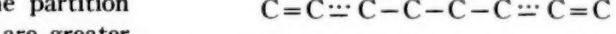
Since the numerical values of the partition functions of such modes of motion are greater than those of vibration of a reasonable frequency, an increase of the calculated rate constant must result. Without going into detailed calculations, the value of which is minimized by the many inherent uncertainties, the following considerations will clarify the point. Evaluating Eyring's expression for a bimolecular rate constant in which only translational (6 for the reactants, 4 for the complex) and external rotational (6 for the reactants, 3 for the complex) degrees of freedom have been included, Pauling's values for internuclear distances being used throughout, one finds a value of *ca.* $10^5 \exp(-E'/RT)$ with insignificant variations from one reaction to another in the group considered. The activation energy E' is at the "experimental" temperature but again only the external degrees of freedom have been included in the correction from absolute zero. The experimental A factors are some 10^3 to 10^5 times larger than the above value. These factors must be interpreted by considering the remaining internal degrees of freedom of which the product has more than the reactants.

In the cyclic activated complex, as seen in the following diagram, there is one internal free rotation (2–3) against two (2–3, 6–7) in the reactant molecules:



The complex has six more vibrations than the two reactant molecules together. Hence, in the first approximation,[55] the ratio of the product of six vibrational partition functions to one internal rotation function must have values up to 10^5—whence the low frequencies calculated by Kistiakowsky and Lacher.[9]

In the case of the free radical intermediate:



the complex has three internal rotations, around bonds 3–4, 4–5, and 5–6. Probably no rotations are possible around the other bonds because of resonance. The complex has four more vibrations than the two reactants together and the additional factor in the rate expression, in the first approximation, equals the product of four vibrational functions times an internal rotation partition function. This latter is numerically equal to 25–100 for the different molecules here considered and hence only a relatively small residual factor needs to be assigned to the vibrational partition functions. Furthermore, since the structure of the complex is that of an open chain, lower frequencies of vibration are to be expected and so the difficulty disappears altogether.

While the explanation here offered is satisfactory in a semi-quantitative way, it fails to explain as yet the differences in the A factors found for the several reactions studied. Perhaps such an explanation cannot even be hoped for with our present inadequate knowledge of the reaction mechanism, but some suggestions can be offered in the hope that they may lead to more exact calculations in the future. As has been shown in several recent publications,[56–58] the assumption of internal free rotation leads to too high entropy values for saturated hydrocarbons. Hence in the present calculations, numerically smaller partition functions should also be used. The extent of the lowering, however, is uncertain and undoubtedly it would be incorrect to assume that it is the same for the several structures considered. Thus, in 1,3-butadiene—and other conjugated diene hydrocarbons—a resonance energy between the double bonds has been found which amounts to some 3 Cal. per mole.[14] This resonance tends to keep the double bonds in a plane and hence offers additional hindrance to free rotation above that which is due to causes operative in saturated hydrocarbons.

[55] In which vibrational (or rotational) partition functions in the denominator of the rate expression are assumed to cancel an equal number of vibrational (or rotational) functions in the numerator.

[56] Smith and Vaughan, J. Chem. Phys. **3**, 341 (1935).
[57] Aston, ibid. **4**, 391 (1936).
[58] Kemp and Pitzer, ibid. **4**, 749 (1936); J. Am. Chem. Soc. **59**, 276 (1937).

It is possible that this effect may cause the denominator of the rate expression in 1,3-butadiene polymerization to be smaller than that in the Diels-Alder condensations thereby explaining the experimental differences in the A factors; however, in acrolein or crotonaldehyde the experimental resonance energy is hardly smaller than in 1,3-butadiene (work from this laboratory to be published in the near future). The activated complexes in the two groups of reactions are so similar—differing only in side structures which do not take an active part in the reaction—that one meets considerable difficulty in trying to find a reasonable explanation of the observed difference. But the same difficulty arises with the cyclic complex and so this point cannot decide the issue.

The polymerization of cyclopentadiene is better suited to a numerical calculation because of lesser uncertainties due to internal rotations. Using the tricyclic dimer with conventional internuclear distances for the model of the activated complex, one finds for the average frequency of the six new vibrations $\nu \leqq 150$ cm^{-1}, while the free radical model leads to $\nu \leqq 450$ cm^{-1} in the approximation defined in reference 55. This latter figure is to be lowered if there is no free rotation around the single bond joining the two rings and in any case is much more reasonable than the other.[43] Qualitatively one can explain why the A factor of this reaction is smaller than those of other diene reactions: long straight chains are formed there with resultant lowering of the vibrational frequencies, whereas here the two rings retain their dynamic independence fairly well and hence have essentially the same frequencies as before the reaction.[59]

It may be pointed out that for most of the organic compounds which are known to polymerize readily, free radical intermediates, stabilized by resonance, can be constructed. It is therefore probable that this particular mechanism has a greater range of application than merely in diene polymerization and Diels-Alder condensation.

[59] If the new work of Khambata and Wassermann (reference 42) is correct, the cyclopentadiene reaction is more similar to the Diels-Alder reactions. The explanation as given is still applicable for this particular reaction.

In having outlined these interpretations we are fully aware of their crudeness and approximate character. However, the essential point to be noted is that the use of cyclic intermediary complexes does not reduce the difficulties of interpretation but actually increases them greatly. Because of this and of other evidence, we believe the free radical mechanism in these polymerizations to be more probable.

We are indebted to Dr. William E. Vaughan of this laboratory for several valuable suggestions and for assistance with some of the measurements.

Summary

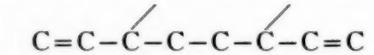
Dimerizations of styrene, vinyl acetylene, chloroprene, vinyl acetate, allene, cyclopentadiene, 1,3-pentadiene and 2,3-dimethyl butadiene-1,3 have been studied in the gas phase. Only the last three reactions give clean-cut results; their rate data can be represented by:

1,3-pentadiene
$k = 3.5 \times 10^{10} \exp(-26000/RT)$ cc mole^{-1} sec.$^{-1}$
2,3-dimethyl butadiene-1,3
$k = 1.4 \times 10^{10} \exp(-25300/RT)$ cc mole^{-1} sec.$^{-1}$
cyclopentadiene
$k = 8.5 \times 10^{7} \exp(-14900/RT)$ cc mole^{-1} sec.$^{-1}$.

The dimerization of the last compound has also been studied in the pure liquid phase and in tetrahydronaphthalene solution. The rates can be represented by the equations: $k = 2.0 \times 10^{9} \exp(-17100/RT)$ and $k = 4.2 \times 10^{9} \exp(-17300/RT)$ cc mole^{-1} sec.$^{-1}$.

The depolymerization of dicyclopentadiene has been studied in the gas phase. The reaction is unimolecular and the rate may be expressed by: $k = 1.0 \times 10^{13} \exp(-33700/RT)$ sec.$^{-1}$.

The kinetics of the gas phase polymerizations and Diels-Alder condensations are discussed and it is concluded that they occur through the mechanism of free radicals. In the case of 1,3-butadiene the radical has the structure:



which is stabilized by resonance between four possible electronic structures.

Calculation of the Energy of H_3 and of H_3^+. III

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In previous communications, the energy of the triatomic hydrogen molecule and of the triatomic positive ion was calculated by the variational method for the symmetrical linear configurations. In this paper, these energies are obtained for two unsymmetrical linear configurations using the most general eigenfunction which can be formed out of 1*s* hydrogen-like atomic orbitals. Two of the four difficult exchange integrals which involve the coordinates of three nuclei are obtained in closed form. For the Wang plus polar states approximation, the activated state for the reaction $H+H_2$ is found to be linear symmetrical whereas the semi-empirical calculations give an unsymmetrical activated state. The complete potential energy surface for three hydrogen atoms on a line is constructed, for this Wang plus polar states approximation. The energy of the triatomic positive ion is likewise lowest for the linear symmetrical. The complete energy surface of H_2+H^+ in a line is constructed and the vibration frequencies computed. The frequency of the linear symmetrical vibration for H_3^+ is 1.4×10^{14} wave no. per sec. and the frequency of the linear unsymmetrical vibration is 1.2×10^{14}.

INTRODUCTION

IN previous communications,[1,2] the energy of the triatomic hydrogen molecule and of the triatomic positive ion was calculated by the variational method for the symmetrical linear configurations. In this paper, these energies are obtained for two linear unsymmetrical configurations. Using these results, we locate the activated state for the reaction $H+H_2$ as the symmetrical linear configuration, whereas the semi-empirical calculations give an unsymmetrical activated state. The energy for the triatomic positive ion is a minimum for the symmetrical configuration. The linear vibration frequencies are calculated.

I. H_3, the triatomic hydrogen molecule

The triatomic hydrogen molecule is the metastable molecule which is formed instantaneously in the reaction of a hydrogen (or deuterium) atom with a hydrogen molecule. A knowledge of the energy of this molecule for various configurations of the nuclei is sufficient for the calculation of the absolute rate of the 10 different reactions of either H or D with H_2 *ortho* or *para*, HD, and D_2 *ortho* or *para*[3]. The semi-empirical scheme for calculating the energy surfaces gives excellent agreement with the experimentally observed rates of reaction. The justification of this method is still largely empirical so that the present investigation was undertaken to obtain results by means of the rigorous quantum-mechanical variational principle using as complicated an eigenfunction as was consistent with the evaluation of all the integrals. The treatment is restricted to forms for the eigenfunction such that the integrals of the mutual electronic repulsions can be computed. We use here the most general charge distribution which can be made up from hydrogen-like 1*s* eigenfunctions. This is a linear combination of two homopolar and six polar states.

$$\Psi=a_1\psi_1+a_2\psi_2+a_3\psi_3+a_4\psi_4+a_5\psi_5+a_6\psi_6+a_7\psi_7+a_8\psi_8.$$

The homopolar states are:

$$\psi_1=\begin{pmatrix}abc\\ \alpha\beta\alpha\end{pmatrix}-\begin{pmatrix}abc\\ \beta\alpha\alpha\end{pmatrix},$$

corresponding to a valence bond between a and b and

$$\psi_2=\begin{pmatrix}abc\\ \alpha\beta\alpha\end{pmatrix}-\begin{pmatrix}abc\\ \alpha\alpha\beta\end{pmatrix},$$

corresponding to a valence bond between b and c. Here the quantity in parentheses indicates the usual Slater determinants and α and β are the two eigenfunctions corresponding to the eigenvalues $h/4\pi$ and $-h/4\pi$ for the z components of spin. The third possible homopolar bonding function,

[1] Hirschfelder, Eyring, Rosen, J. Chem. Phys. **4**, 121 (1936).
[2] Hirschfelder, Eyring, Rosen, J. Chem. Phys. **4**, 130 (1936).
[3] Hirschfelder, Eyring, Topley, J. Chem. Phys. **4**, 170 (1936).

i.e., a bond between a and c, is a linear combination of these two and therefore is not considered explicitly. The polar functions are:

$$\psi_3=\begin{pmatrix} bbc \\ \alpha\beta\alpha \end{pmatrix}, \text{ two electrons on } b, \text{ one on } c$$

$$\psi_4=\begin{pmatrix} bba \\ \alpha\beta\alpha \end{pmatrix}, \text{ " " " } b, \text{ " " } a$$

$$\psi_5=\begin{pmatrix} aab \\ \alpha\beta\alpha \end{pmatrix}, \text{ " " " } a, \text{ " " } b$$

$$\psi_6=\begin{pmatrix} ccb \\ \alpha\beta\alpha \end{pmatrix}, \text{ " " " } c, \text{ " " } b$$

$$\psi_7=\begin{pmatrix} aac \\ \alpha\beta\alpha \end{pmatrix}, \text{ " " " } a, \text{ " " } c$$

$$\psi_8=\begin{pmatrix} cca \\ \alpha\beta\alpha \end{pmatrix}, \text{ " " " } c, \text{ " " } a$$

For the symmetrical case previously considered, it was possible to take linear combinations of these states which were either symmetric or antisymmetric in the nuclei a and c, and since the Hamiltonian in this case was symmetric in these nuclei, the four symmetrical and the four antisymmetrical combinations were mutually noncombining. For the unsymmetrical linear configurations there is no such simplification and it is necessary to vary the composition of our best eigenfunction by varying the $a_1, a_2, \cdots, a_8$ separately. This corresponds to the Heitler-London plus polar states type of approximation. A better charge distribution is obtained by varying the effective nuclear charge in these eigenfunctions as well as the polar-homopolar composition. This variation of the effective nuclear charge does not involve the evaluation of any further integrals and is carried out readily.

The method of calculation is in every way similar to that which was used[4] in the case of the linear symmetrical H_3 and H_3^+. For the Wang plus polar states type of approximation, the best value of the energy E_z for a given value of the screening constant (or effective nuclear charge) z is the solution of the secular equation:

$$|H_{ij}-S_{ij}E_z|=0.$$

[4] The method of calculation is explained in considerable detail in the first paper of this series (J. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. **4**, 121 (1936)). All of the intermediate steps and numerical data for the linear symmetrical case are given in the Dissertation of J. Hirschfelder, Princeton University (1935). The authors will be glad to furnish on request similar information for this linear unsymmetrical problem.

Here

$$H_{ij}=\int \bar{\psi}_i H\psi_j d\tau, \qquad i, j=1, 2, \cdots, 8,$$

$$S_{ij}=\int \bar{\psi}_i\psi_j d\tau,$$

and H is the operator for the sum of the kinetic energy for the electrons, the energy of mutual repulsion of the nuclei, the energy of attraction of the electrons to the nuclei, and the energy of mutual repulsion of the electrons. By solving this secular equation for a number of different values of z, we were able to obtain the best linear combination of the eight different electronic states for the best value of the effective nuclear charge. The integrals, H_{ij}, are the sum of a great many terms which arise from expanding the Slater determinants of the bond eigenfunction, ψ_j, operating on it by the many parts of the Hamiltonian operator, and multiplying this resultant by the Slater determinants of the other eigenfunction, ψ_i. The only terms in these energy integrals which are difficult to evaluate arise from the mutual repulsions of the electrons. These difficult integrals are treated in the appendix. All of the other integrals which appear have been previously considered.[1, 2]

In this paper, we calculate the energy for two nuclear configurations:

$$r_{ab}=2.0a_0/z, \quad r_{bc}=2.5a_0/z \tag{1}$$

and

$$r_{ab}=1.5a_0/z, \quad r_{bc}=2.5a_0/z. \tag{2}$$

Here a_0 and z are the Bohr radius and the effective nuclear charge respectively; r_{ab} and r_{bc} are the separations of atoms a to b and b to c, respectively. Table I shows the energies which we obtained for these configurations and compares them with the energies for linear symmetrical configurations previously considered.[1] The Heitler-London and the Wang types of approximations are obtained by considering only the homopolar eigenfunctions. The former corresponds to an effective nuclear charge of unity, the latter to the effective nuclear charge which gives the lowest value for the energy. The best values which we obtain for the energy are computed for the Wang plus polar states approximation. Fig. 1 shows the entire potential energy surface for an H atom

TABLE I. *Energy of H_3 (zero of energy for three infinitely separated H atoms).*

	H.L.	H.L. PLUS POLAR	WANG	WANG POLAR
Unsymmetrical Configurations				
(1) $r_{ab}=2.0a_0/z$, $r_{bc}=2.5a_0/z$	53.44 kcal.	60.38 kcal.	57.23 ($z=1.066$)	68.68 ($z=1.102$)
(2) $r_{ab}=1.5a_0/z$, $r_{bc}=2.5a_0/z$	54.70	58.45	57.56 ($z=1.0565$)	64.0 ($z=1.10$)
Symmetrical Configurations (previously considered[1])				
(1) $r_{ab}=2.5a_0/z$, $r_{bc}=2.5a_0/z$	44.06	51.04	47.34 ($z=1.061$)	58.84 ($z=1.097$)
(2) $r_{ab}=2.0a_0/z$, $r_{bc}=2.0a_0/z$	53.11	60.39	56.16 ($z=1.059$)	67.09 ($z=1.087$)
(3) $r_{ab}=1.5a_0/z$, $r_{bc}=1.5a_0/z$	14.99	22.79	14.99 ($z=1.001$)	23.69 ($z=1.034$)
Binding Energy of H_2 (for reference purposes)				
(Sugiura*) $r_{ab}=1.65a_0$	72.18			
(Wang**) $r_{ab}=1.70a_0$		74.02		
(Weinbaum†) $r_{ab}=1.38a_0$			86.94 ($z=1.166$)	
(Weinbaum†) $r_{ab}=1.42a_0$				92.24 ($z=1.193$)

* Y. Sugiura, Zeits. f. Physik **45**, 484 (1927).
** S. C. Wang, Phys. Rev. **31**, 579 (1928).
† S. Weinbaum, J. Chem. Phys. **1**, 593 (1933).

reacting with an H_2 molecule computed for this approximation. The symmetrical configuration $r_{ab}=r_{bc}=1.84a_0=0.97$A is the activated state. The atoms in the activated state are spread farther apart than in the normal H_2 molecule where $r_{ab}=0.74$A. This expansion is also obtained from semi-empirical calculations. There is one feature of our results which is surprising. The semi-empirical scheme predicts that the activated state will correspond to an unsymmetrical arrangement of the atoms and that the energy will decrease as the atoms go from such an unsymmetrical array to the lowest symmetrical configuration. The calculation of the rates of the reactions will not be essentially changed by this symmetry of the activated configuration. We have a transmission coefficient of unity in the symmetrical case, i.e., all of the molecules reaching the activated state react, but the symmetry number compensates this increase by reducing the number of activated states by a factor of two. When the activated state is unsymmetrical, the transmission coefficient is a half and the symmetry factor is unity. Thus the statistics are not altered. The actual values of the energy which we obtain are not sufficiently accurate, due to the faulty charge distribution, to be used for reaction rate calculations. The frequency of the vibration in which the linear symmetry of the nuclei is preserved is:

$$\nu_s=9.5\times10^{13}\ \text{sec.}^{-1},\quad h\nu_s=9.0\ \text{kcal.}$$

The activated complex in a chemical reaction is a good example of the resonance phenomenon. The molecules start with one type of bonds in the beginning of the reaction and finish the reaction with another set of bonds. The activated complex corresponds then to a mixture of the two types, the energy is considerably lower for the mixture than it would be for either one separately. As the atoms come closer together the polar states assume greater importance. Thus unsymmetrical activated states possess large dipole

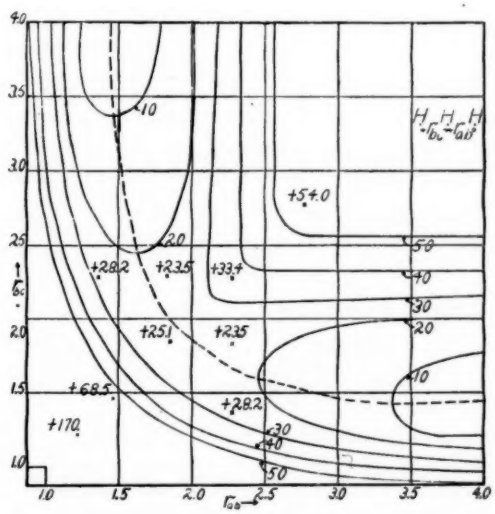

FIG. 1. Energy surface for three hydrogen atoms in a line to the Wang plus polar states approximation. Energies are given in kcal. and distances in Bohr radii.

moments as is exemplified by the polar states in H_3. A specific example will illustrate this resonance phenomenon. In Fig. 2 the reaction between

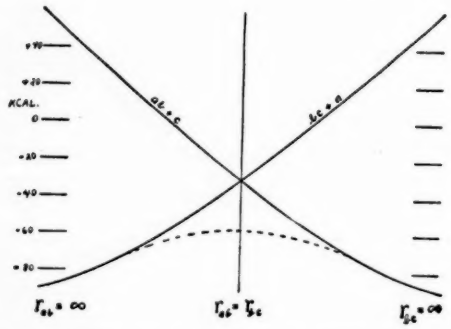

FIG. 2. The energy to the Wang approximation of a deuterium or hydrogen atom, a, approaching a hydrogen molecule, bc. The curves $ab-c$ and $bc-a$ are the energies of the system for the pure bond states. The dotted line is the energy for the best linear combination of the pure bond states.

a D atom, "c," and the H_2 molecule composed of atoms "a" and "b" is considered using the Wang approximation. The "best" eigenfunction for the molecule composed of three atoms can be written:

$$\Psi = A_{ab}\psi_{ab} + A_{bc}\psi_{bc},$$

where ψ_{ab} and ψ_{bc} are bond eigenfunctions each normalized to unity. When the chemical reaction begins, atom c is far away,

$$\Psi = \psi_{ab}, \quad E = E_{ab}$$

and there is no resonance between the bonds ab and bc. When the atom c has penetrated sufficiently near to a and b, the "best" eigenfunction is the combination of states (1) and (2) which gives the greatest binding energy, i.e., minimum potential energy. This energy is lower than for either of the pure bond states. Thus when

$$r_{ab} = 1.876a_0 \quad \text{and} \quad r_{bc} = 2.345a_0,$$
$$A_{ab} = .7645 \qquad A_{bc} = .3084,$$

$E = -57.23$ kcal. but $E_{ab} = -48.91$ and $E_{bc} = -6.06$

and when

$$r_{ab} = 1.420a_0 \quad \text{and} \quad r_{bc} = 2.366a_0,$$
$$A_{ab} = 0.875 \qquad A_{bc} = 0.160,$$

$E = -57.56$ kcal. but $E_{ab} = -54.52$ and $E_{bc} = +34.03$.

Finally when the distance ab is equal to that of bc, $A_{ab} = A_{bc}$. We see that the character of the valence bond in a chemical reaction does not change appreciably until the atoms are very close to the activated state, and it is there that resonance plays an important role.

It is sometimes supposed that states showing a large degree of resonance are necessarily states of low energy. The activated state is an example where the contrary is true since the comparatively pure initial and final bond states have much lower energies. This situation arises in the following way. Bonding is increased if the electrons have many nuclei about which they can circulate since this lowers the zero point energy of the electrons. Acting against this bonding are the mutual repulsions between the electrons and between the nuclei. In general then for a given nuclear configuration resonance lowers the bonding energy but the system will very often sacrifice this resonance and move into a pure bonding state with the full quota of saturated bonds if by so doing it can sufficiently lower the nuclear repulsion.

A further question which one might ask is how sensitive is the binding energy to the screening constant or to the effective nuclear charge, z,

TABLE II. *Energy of H_3^+. (The zero of energy is taken for the two hydrogen atoms and the proton separated infinitely far apart.)*

	HEITLER-LONDON PLUS POLAR STATES	WANG PLUS POLAR STATES
Unsymmetrical Configurations		
(1) $r_{ab} = 2.0a_0/z$, $r_{bc} = 2.5a_0/z$	−105.4 kcal.	−151.0 kcal. ($z = 1.32$)
(2) $r_{ab} = 1.5a_0/z$, $r_{bc} = 2.5a_0/z$	−94.0	−129.8 ($z = 1.30$)
Symmetrical Configurations (previously considered[2])		
(1) $r_{ab} = r_{bc} = 2.5a_0/z$	−96.8	−138.1 ($z = 1.30$)
(2) $r_{ab} = r_{bc} = 2.0a_0/z$	−108.6	−155.4 ($z = 1.31$)
(3) $r_{ab} = r_{bc} = 1.5a_0/z$	−78.3	−101.3 ($z = 1.22$)

which is used in the eigenfunctions. When z is very different from its best value, as for example the Heitler-London type of approximation where z is equal to unity, the energy of binding changes rapidly with z; but when z is in the neighborhood of its best value, a change of 0.02 increases the energy by about 0.2 kcal.

H_3^+, triatomic positive ion

The triatomic hydrogen positive ion, H_3^+, is observed in the mass spectrograph when hydrogen gas is ionized at reasonably high pressures.[2] There is reason to believe that it is formed in three ways:

$$H^+ + H_2 \rightarrow H_3^+ \quad (1)$$

$$H + H_2^+ \rightarrow H_3^+ \quad (2)$$

$$H_2 + H_2^+ \rightarrow H_3^+ + H. \quad (3)$$

Experiments tell us no more as to the energy, spectrum, or chemistry of H_3^+. However, we may use the rigorous quantum mechanical variational principle to calculate the energy for various configurations of the triatomic ion as we did for the triatomic molecule. The energy for symmetrical linear configurations was treated in a previous paper. Unsymmetrical linear configurations are considered here and with them we are able to draw the energy surface either for a hydrogen ion approaching a hydrogen molecule, i.e., reaction (1), or for a hydrogen atom approaching a diatomic hydrogen ion, i.e., reaction (2). The integrals which are necessary for the computations are the same as those for the triatomic molecule and are considered in the appendix. We use for the eigenfunctions the most general linear combination of the three polar and the three homopolar eigenfunctions which can be obtained from hydrogen-like $1s$ eigenfunctions. The six parameters governing the composition of our eigenfunction are varied simultaneously to give the lowest energy, i.e., Heitler-London plus polar states type of approximation. To obtain an even better charge distribution we vary the effective nuclear charges at the same time as the composition, i.e., Wang plus polar states type of approximation. In the eigenfunctions the polar state with two electrons on the central atom is just as important as the homopolar states. Table II shows the results which we obtained. The energy for these configurations enables us to calculate the frequency of the linear symmetrical vibration ν_s and the linear unsymmetrical vibration ν_l:

$$\nu_s = 1.4 \times 10^{14}, \quad h\nu_s = 13 \text{ kcal.}$$
$$\nu_l = 1.2 \times 10^{14}, \quad h\nu_l = 12 \text{ kcal.}$$

We can use the polarizabilities, α, of H_2, H, and H_2^+ to calculate the energy of reactions (1)

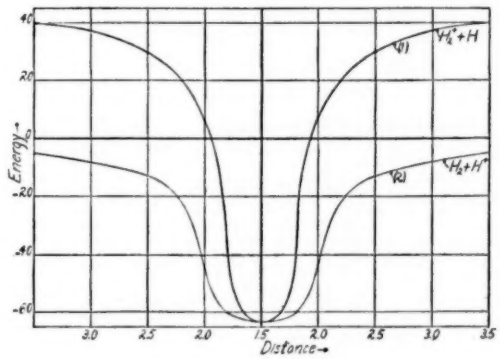

FIG. 3. (1) Energy of an H atom approaching H_2^+ in a line as a function of the separation between the H and the H_2^+. (2) Energy of a proton approaching H_2 in a line as a function of the distance between the H^+ and the H_2. Energies are given in kcal. and distances in Bohr radii.

and (2) for large distances. Let us consider reaction (1). The molecule H_2 is polarized by the field of the H and attracted to it with a force whose potential is:

$$E_{H_2+H^+} = -\frac{\alpha_{H_2} e^2}{2R^4}$$

where R is the separation between H^+ and the center of the hydrogen molecule. The experimental mean value for α_{H_2} is $.8 \times 10^{-24}$ cm^3 $= 5.4a_0^3$. α_{mean} is used rather than $\alpha_{parallel}$ since the polarizing field of the H^+ is spherical rather than plane for the interesting separations. Fig. 3 shows the energies of $H + H_2^+$ and $H_2 + H^+$ plotted as a function of the separation. For large separations the $H_2 + H^+$ has about 44 kcal. less energy than the $H_2^+ + H$. At closer distances, the interaction energy between the ion and the molecule or atom is determined by the polarizabilities. And at the closest distance of approach, $1.5a_0$, the energy of the H_3^+ is the same regardless of whether it originated from $H_2^+ + H$ or $H_2 + H^+$. It is surprising that the energy of H_3^+ is nearly equal to the electrostatic energy $\alpha_{H_2} e^2/2R^4$ for the appropriate value of R. This equality is partly

accidental since there are other types of important interactions between H_2 and H^+. However, we can use this ion-polarization energy to help us draw the contour lines in the energy surface for an H^+ approaching an H_2 molecule, Fig. 4. Here

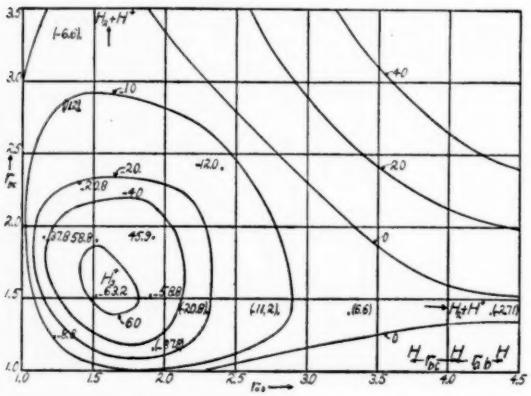

FIG. 4. Energy surface for a system of two hydrogen atoms and a proton. The position of minimum energy corresponds to H_3^+. Energies are given in kcal. and distances in Bohr radii.

we see that the H^+ is attracted to the H_2 until the nuclei are equally spaced. The equal potential surfaces for the H_3^+ are approximately circular. The numbers given in this figure are the values of the energy which have been calculated to the Wang-plus-polar-states approximation. The numbers given in parentheses are the energies for this ion-polarization attraction. The triatomic molecule corresponds to a symmetrical linear configuration with a minimum of energy for $r_{ab}=r_{bc}=1.6a_0$. The energy of binding of the two hydrogen atoms and the proton is more than 155 kcal., which is sufficient to make reactions (1) and (2) exothermic and make it probable that (3) takes place without an appreciable activation energy.

The energy surface for an H atom approaching an H_2^+ ion is similar to the case just considered since the energies for the H_3^+ at intermediate and close distances are the same as before. However, the minimum energy for the H_2^+ when the H is far away corresponds to the separation of $2.0a_0$ which is considerably more expanded than the separation in H_2. Since the binding energy of H_2^+ is only around 60 kcal., the contour lines will be steeper than for the H_2. The ion-polarization energy in this case is:

$$E_{(H_2^++H)}=-\left[\frac{\alpha_H}{2R^4}+\frac{4(\bar{\alpha}_{H_2^+})(\alpha_H)^2e^2}{R^{10}}\right],$$

where $\bar{\alpha}_{H_2^+}=2.85a_0^3$ and $\alpha_H=4.5a_0^3$ are the polarizabilities of H_2 and H, respectively. While this energy is correct for large separations it is not accurate for the smaller internuclear distances.

INTEGRALS

The integrals for the unsymmetrical linear configuration are of the same order of difficulty as those which have already been considered for the symmetrical linear case. There are four integrals arising from the mutual repulsion of two electrons which we shall consider here. Two of these are integrated in closed form. The other two integrals are evaluated numerically. The mathematical treatment of the integrals is not changed in any essential manner by the lack of symmetry with respect to the nuclei.

I. $L(bb, ac)$ $\quad a \bullet \quad r_{ab} \quad b \bullet \quad r_{bc} \quad c \bullet$

The integral,

$$L(bb, ac)\equiv 1/\pi^2\int\int(1/r_{12})e^{-2r_{1b}-r_{2a}-r_{2c}}d\tau_1 d\tau_2$$

is integrated in closed form as for the symmetrical configuration. The integration over the coordinates of electron 1 keeping electron 2 fixed is easily performed. This gives:

$$L(bb, ac)=K(b, ac)-T(b, ac)$$

where

$$K(b, ac)\equiv 1/\pi\int(1/r_b)e^{-r_a-r_c}d\tau,$$

$$T(b, ac)\equiv 1/\pi\int(1+1/r_b)e^{-2r_b-r_a-r_c}d\tau.$$

The first integral, $K(b, ac)$, has been previously discussed[1] and offers no difficulty. The second, $T(b, ac)$, can be integrated by introducing the ellipsoidal coordinates with foci at a and at c:

$$\lambda=\frac{r_a+r_c}{r_{ac}},\quad \mu=\frac{r_a-r_c}{r_{ac}},\quad \phi$$

The parameter $A=(r_{ab}-r_{bc})/r_{ac}$ is a measure of the asymmetry of the molecule.

$$T(b, ac)=\frac{r_{ac}^3}{4}\int_1^\infty\int_{-1}^1(\lambda^2-\mu^2)\left[1+\frac{2}{r_{ac}(\mu^2+\lambda^2-2A\mu\lambda+A^2-1)^{\frac{1}{2}}}\right]$$
$$\times\exp\left(-r_{ac}[\lambda+(\mu^2+\lambda^2-2A\mu\lambda+A^2-1)^{\frac{1}{2}}]d\mu d\lambda.\right.$$

The substitution of $X=2\lambda-2A\mu+2(\mu^2+\lambda^2-2A\mu\lambda+(A^2-1))^{\frac{1}{2}}$ for λ rationalizes the integral, since

$$\lambda=X/4+A\mu+[(A^2-1)(\mu^2-1)]/X^2.$$

There are two limits of integration for X depending on whether A is greater or less than μ. The problem is then resolved into the integration of a large number of simple integrals. We obtain:

$$T(b, ac)=a_1e^{+(A-2)r_{ac}}+a_2e^{-(A+2)r_{ac}}+a_3e^{-r_{ac}}+a_4e^{-Ar_{ac}}[Ei(-(1-A)r_{ac})-Ei(-2r_{ac}(1-A))$$
$$-Ei(-2r_{ac})]+a_5e^{+Ar_{ac}}[Ei(-(1+A)r_{ac})-Ei(-2r_{ac}(1+A))-Ei(-2r_{ac})],$$

where

$$a_1=-(1/8)A^{-4}(A^2-1)(A^2-A-2)r_{ac}+[3/16+A^{-1}+(15/16)A^{-2}-(5/8)A^{-3}-(5/8)A^{-4}]$$
$$+r^{-1}_{ac}[-A^{-1}-3A^{-2}+(57/16)A^{-3}+(31/4)A^{-4}-(15/8)A^{-5}-(15/4)A^{-6}],$$
$$a_2=-(1/8)A^{-4}(A^2-1)(A^2+A-2)r_{ac}+[3/16-A^{-1}+(15/16)A^{-2}+(5/8)A^{-3}-(5/8)A^{-4}]$$
$$+r^{-1}_{ac}(A^{-1}-3A^{-2}-(57/16)A^{-3}+(31/4)A^{-4}+(15/8)A^{-5}-(15/4)A^{-6})],$$
$$a_3=-(1/2)A^{-4}(A^2-1)r_{ac}+[2-(9/2)A^{-2}+(5/2)A^{-4}]+r^{-1}_{ac}[6A^{-2}-(31/2)A^{-4}+(15/2)A^{-6}],$$
$$a_4=(1/4)A^{-7}(A^2-1)[A^3(A^2-1)r^2_{ac}+2A^2(4A^2-3)r_{ac}+3(7A^2-5)(A+r^{-1}_{ac})],$$
$$a_5=(1/4)A^{-7}(A^2-1)[A^3(A^2-1)r^2_{ac}-2A^2(4A^2-3)r_{ac}+3(7A^2-5)(A-r^{-1}_{ac})].$$

Here $Ei(-X)$ is the integral logarithm,

$$Ei(-X)=-\int_X^\infty(e^{-X}/X)dX,$$

and it is tabulated[5] in a number of different books. Setting $A=0$, we obtain the value for the symmetrical case which we considered previously. Or setting $A=\pm1$, which corresponds to coalescence of b and either a or c, $T(b, ac)$ degenerates into a simple two center integral and provides a further check on the validity of our result.

II. $L(aa, bc)$ or $L(cc, ba)$

$$L(aa, bc)\equiv1/\pi^2\int\int1/r_{12}e^{-2r_{a1}-r_{b2}-r_{c2}}d\tau_1d\tau_2.$$

This integral is somewhat similar to $L(bb, ac)$. We can integrate over the coordinates of electron one and obtain:

$$L(aa, bc)=K(a, bc)-T(a, bc),$$

$$K(a, bc)=1/\pi\int1/r_ae^{-r_b-r_c}d\tau,$$

$$T(a, bc)=1/\pi\int(1+1/r_a)e^{-2r_a-r_b-r_c}d\tau,$$

[5] Cf. Jahnke-Emde, *Funktionentafeln* (Teubner 1933), p. 78.

where again $K(a, bc)$ is an integral considered previously and $T(a, bc)$ is the difficult integral which must be evaluated. Using ellipsoidal coordinates with foci at b and at c and setting $B=1+2(r_{ab}/r_{bc})$

$$T(a, bc)=\frac{r^3_{bc}}{4}\int_1^\infty\int_{-1}^1(\lambda^2-\mu^2)\left[1+\frac{2}{r_{bc}(\lambda^2+\mu^2-2B\mu\lambda+B^2-1)^{\frac{1}{2}}}\right]$$
$$\times\exp\left(-r_{bc}[\lambda+(\lambda^2+\mu^2-2B\mu\lambda+B^2-1)^{\frac{1}{2}}]\right)d\mu d\lambda.$$

Substituting $X=2\lambda-2B\mu+2(\mu^2+\lambda^2-2B\mu\lambda+B^2-1)^{\frac{1}{2}}$ in place of λ, the integrand is rationalized. There is only one range of integration for X and the integrations may be performed without any serious difficulty. We obtain:

$$T(a, bc)=(1/48)[b_1e^{-Br_{bc}}+b_2e^{-(B+2)r_{bc}}+b_3e^{Br_{bc}}Ei(-2(B+1)r_{bc})+b_4e^{-Br_{bc}}[Ei(-2r_{bc})+\log(B+1)]],$$

where

$$b_1=B^{-3}(2B^5+12B^3-20B^2-6B+12)r^2_{bc}+B^{-4}(18B^5+24B^4+66B^3-144B^2-36B+72)r_{bc}$$
$$+B^{-5}(9B^5+144B^4+171B^3-372B^2-90B+180)$$
$$+B^{-6}(-48B^5+144B^4+171B^3-372B^2-90B+180)r^{-1}_{bc},$$

$$b_2=B^{-4}(-6B^4-6B^3+18B^2+6B-12)r_{bc}+B^{-4}(9B^4-48B^3+45B^2+30B-30)$$
$$+B^{-6}(48B^5-144B^4-171B^3+372B^2+90B-180)r^{-1}_{bc},$$

$$b_3=-12B^{-7}(B^2-1)[B^3(B^2-1)r^2_{bc}-2B^2(4B^2-3)r_{bc}+3(7B^2-5)(B-r^{-1}_{bc})],$$

$$b_4=-12B^{-7}(B^2-1)[B^3(B^2-1)r^2_{bc}+2B^2(4B^2-3)r_{bc}+3(7B^2-5)(B+r^{-1}_{bc})].$$

$T(a, bc)$ reduces to the symmetrical case for $B=3$ and to the two center integrals corresponding to $r_{ab}=0$ when $B=1$.

III. $L(ab, ac)$, $L(ab, bc)$, $L(bc, ac)$

The integrations over the first electronic coordinates may be carried out for these integrals.

$$L(ab, ac)\begin{cases}=1/\pi^2\int\int 1/r_{12}e^{-r_{a_1}-r_{b_1}-r_{a_2}-r_{c_2}}d\tau_1d\tau_2\\ =1/\pi\int(K(2, ab))e^{-r_{a_2}-r_{c_2}}d\tau_2,\end{cases}$$

$$L(ab, bc)\begin{cases}=1/\pi^2\int\int 1/r_{12}e^{-r_{a_1}-r_{b_1}-r_{b_2}-r_{c_2}}d\tau_1d\tau_2\\ =1/\pi\int K(2, ab)e^{-r_{b_2}-r_{c_2}}d\tau_2.\end{cases}$$

Here

$$K(2, ab)=\frac{1}{\pi}\int 1/r_{12}e^{-r_{a_1}-r_{b_1}}d\tau_1$$

is an integral considered previously.[1] Introducing ellipsoidal coordinates at a and at b and setting

$$C=1+2(r_{bc}/r_{ab}):$$

$$L(ab, ac)=\frac{r^3_{ab}}{4}\int_1^\infty\int_{-1}^1[\lambda^2-\mu^2]K(2, ab)\exp\left[-(r_{ab}/2)[\lambda+\mu+(\mu^2+\lambda^2-2C\mu\lambda+C^2-1)^{\frac{1}{2}}]\right]d\mu d\lambda.$$

Also

$$L(ab, bc)=\frac{r^3_{ab}}{4}\int_1^\infty\int_{-1}^1[\lambda^2-\mu^2]K(2, ab)\exp\left[-(r_{ab}/2)[\lambda-\mu+(\mu^2+\lambda^2-2C\mu\lambda+C^2-1)^{\frac{1}{2}}]\right]d\mu d\lambda.$$

Now letting

$$I(\mu, \lambda)=\exp\left[-(r_{ab}/2)[\lambda+\mu+(\lambda^2+\mu^2-2C\mu\lambda+C^2-1)^{\frac{1}{2}}]\right](\lambda^2-\mu^2)K(2, ab).$$

It follows that

$$L(ab, ac)=\frac{r^3_{ab}}{4}\int_{-1}^1\int_1^\infty I(\mu, \lambda)d\lambda d\mu \quad \text{and} \quad L(ab, bc)=\frac{r^3_{ab}}{4}\int_{-1}^1 e^{\mu r_{ab}}d\mu\int_1^\infty I(\mu, \lambda)d\lambda.$$

The family of integrals, $\int_1^\infty I(\mu, \lambda)d\lambda$, are common to both $L(ab, ac)$ and $L(ab, bc)$. These integrals are obtained in closed form for $\mu=\pm 1$, but for other values it is more tractable to evaluate $I(\mu, \lambda)$ by evaluating the integrand at a whole mesh of points and carry out the integrations numerically. The values of $((\partial/\partial\lambda)I(\mu, \lambda))_{\lambda=1}$ are helpful in curve-fitting the integrand.

The actual numerical integration requires extreme care in order to obtain the desired accuracy.The integrand as a function of λ is divided into a large number of overlapping segments. In each of these segments $I(\mu, \lambda)$ is multiplied by $e^{+a\lambda}$ where a is chosen so as to make $e^{+a\lambda}I(\mu, \lambda)$ as nearly constant as possible throughout the segment. Then $e^{a\lambda}I(\mu, \lambda)$ is curve-fitted by a cubic in λ.

$$e^{a\lambda}I(\mu, \lambda)=b_0+b_1\lambda+b_2\lambda^2+b_3\lambda^3.$$

The integration is then performed over a small central part of the segment under consideration.

$$\int_{\lambda_1}^{\lambda_2} I(\mu, \lambda)d\lambda=\int_{\lambda_1}^{\lambda_2} e^{-a\lambda}(b_b+b_1\lambda+b_2\lambda^2+b_3\lambda^3)d\lambda,$$

and the result summed over all of the segments.

The integrations over μ are performed in much the same way except in the neighborhood of $\mu=1$, the integrand has an infinite slope and special precautions taken in order to avoid error in this region.

$L(bc, ac)$ is calculated in the same manner as $L(ab, ac)$ and a second determination of $L(ab, bc)$ is obtained as a by-product. This provides a check on our results since the two values for $L(ab, bc)$ are completely independent. Thus for $r_{ab}=2.0a_0$, $r_{bc}=2.5a_0$: $L(ab, bc)=.09678(e^2/a_0)$ and $.09697(e^2/a_0)$ and for $r_{ab}=1.5a_0$, $r_{bc}=2.5a_0$: $L(ab, bc)=.128, 13(e^2/a_0)$ and $.12760(e^2/a_0)$. The accuracy in both these cases seems to be considerably better than 1 percent and we can probably trust the energies obtained in this text to about 0.2 kcal.

We wish to express our appreciation to the American Philosophical Society for financial assistance.

Vibration Spectra and Molecular Structure. III

The Infrared Absorption Spectra of Cyclopropane and Ethylene Oxide

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(Received June 3, 1937)

With a rocksalt prism spectrometer, the infrared absorption spectra of gaseous cyclopropane and ethylene oxide have been mapped in the region 1–15.5 μ. Cyclopropane shows bands at 6250, 4425, 3086, 2525, 2088, 1887, 1739, 1429, 1021, 860, and 671 cm^{-1}, while ethylene oxide absorbs at 6211, 4310, 3891, 3021, 2632, 2304, 2024, 1733, 1626, 1493, 1255, 1134, 862, 804 and 696 cm^{-1}. In addition to these infrared measurements, a redetermination was made of the Raman spectrum of liquid ethylene oxide. Raman lines appeared at 807, 867, 1123, 1269, 1488, 2914, 2958, and 3007 cm^{-1}.

IN a recent paper[1] the author presented the results of approximate force constant calculations on a number of the simpler organic molecules. In the course of this work it was necessary to obtain the spectra of two of the compounds investigated and it is the purpose of the present article to discuss this experimental work. The infrared absorption spectra of cyclopropane and ethylene oxide vapors were obtained in the region 1–15.5μ and in addition a redetermination was made of the Raman spectrum of liquid ethylene oxide.

APPARATUS AND METHODS

The spectrometer used for the infrared measurements was a low dispersion rocksalt prism instrument, which has already been described.[2]

The light source for Raman effect determinations consisted of two water-cooled Pyrex mercury arcs of the conventional hairpin design, and a saturated sodium nitrite solution was used as filter. This restricted the exciting light essentially to the λ4358A line. A Steinheil high speed three-prism spectrograph was used. This

* National Research Fellow.
[1] L. G. Bonner, J. Chem. Phys. **5**, 293 (1937).
[2] R. B. Barnes, R. R. Brattain, and F. Seitz, Phys. Rev. **48**, 582 (1935).

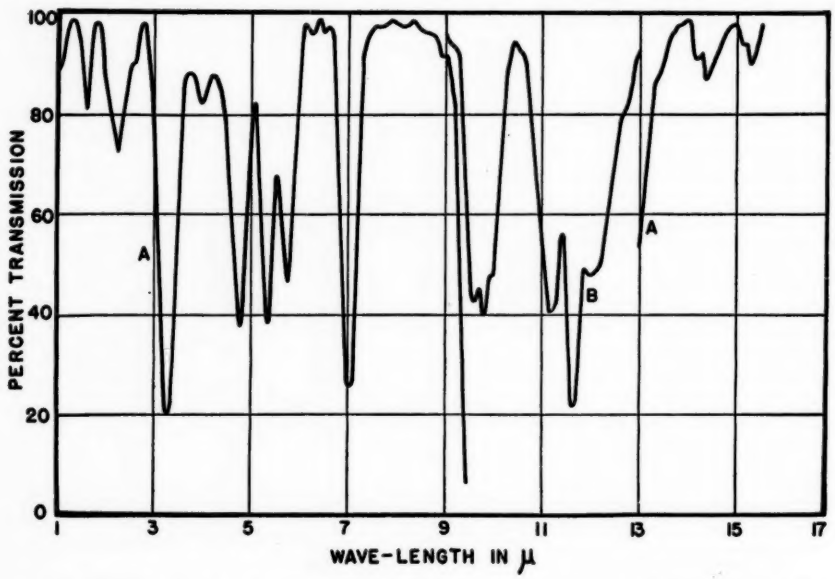

FIG. 1. The absorption of a 15 cm layer of cyclopropane vapor at *A*, 700 mm and *B*, 50 mm pressure.

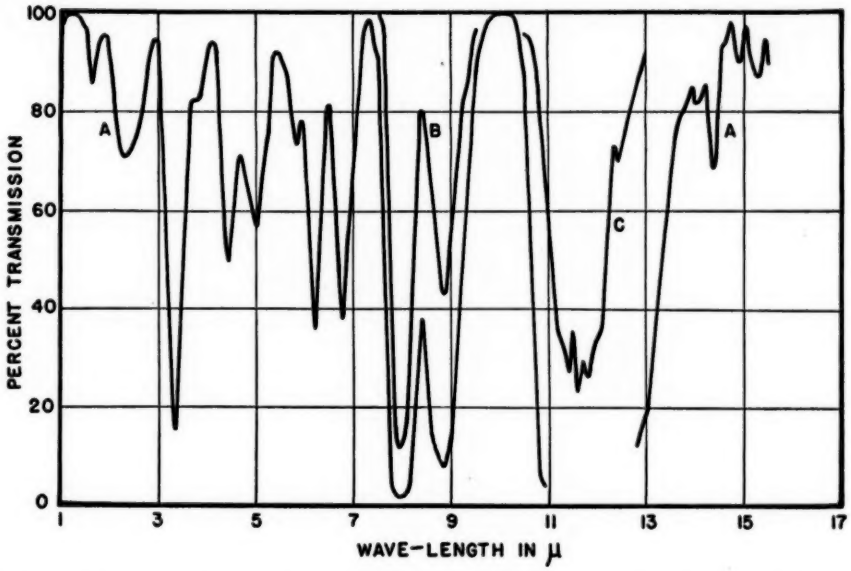

FIG. 2. The absorption of a 15 cm layer of ethylene oxide vapor at *A*, 700 mm, *B*, 200 mm, and *C*, 25 mm pressure.

instrument had a dispersion of about 50A/mm in the region of interest.

In obtaining the infrared curves the fractional transmission of the gas cell was determined at 0.1μ intervals throughout the region 1–15.5μ. In all cases a 15 cm glass cell, sealed at the ends with rocksalt plates, was used. In order to bring out bands with greatest clearness, gas pressures ranging from 25 to 700 mm were used in different spectral regions. After obtaining the above rough curve, the regions of all band centers were gone over again, taking points at 0.02μ intervals in order to locate more accurately the absorption centers, and also to bring out more clearly any structure in the bands.

Since no dummy cell was used in these measurements there was a small and constant background absorption, which was allowed for in the following way. The experimental curve was first plotted, and in this the transmission in regions of no absorption by the gas always reached a definite maximum value, usually 70–80 percent. This was then assumed to be the zero transmission of the cell and the scale of the ordinate changed accordingly.

CYCLOPROPANE

The cyclopropane used in these experiments was a particularly pure product prepared in the Harvard Chemical Laboratories and very kindly supplied to me by Dr. E. Bright Wilson, Jr., for which I wish to thank him at this time. Fig. 1 shows the infrared spectrum of cyclopropane and Table I gives the positions of the band centers, together with the probable accuracy with which they have been determined. The bands at 9.8 and 11.6μ seem to be resolved into *P*, *Q*, and *R* branches, with $P-R$ separations of 42 and 66 cm^{-1} respectively. Due to experimental difficulties, measurements beyond 14μ are somewhat uncertain but there seems to be no doubt about the reality of the two minima at 14.4 and 15.3μ. These may be taken as components of a doublet

TABLE I. *Positions of cyclopropane bands.*

DESCRIPTION	WAVE-LENGTH (μ)	FREQUENCY (cm^{-1})
	1.60	6250± 100
	2.26	4425± 75
	3.24	3086± 20
	3.96	2525± 30
	4.79	2088± 8
	5.30	1887± 7
	5.75	1739± 6
	7.00	1429± 4
R Branch	9.58	1044± 2
Q "	9.79	1021± 2
P "	9.98	1002± 4
R "	11.18	894± 2
Q "	11.63	860± 2
P "	12.07	828± 2
R "	14.4	694± 5
Center	14.9	671± 5
P Branch	15.3	654± 5

type band with center at 14.9μ and a $P-R$ separation of 40 cm^{-1}. For purposes of comparison it is interesting to note that Harris, Ashdown, and Armstrong[3] report Raman lines of cyclopropane at 382, 745, 869, 1022, 1191, 1437, 1454, 1505, 1873, 2856, 2953, 3013, 3030, and 3079 cm^{-1}. The frequencies used in the previous analysis[1] were 869 and 1191 cm^{-1}.

Ethylene Oxide

The material used was a commercial product supplied by the Carbide and Carbon Chemical Company and used without further purification. Fig. 2 shows the infrared spectrum and Table II gives the positions of the band centers. Under higher dispersion the band at 8.0μ seems to resolve into a doublet with center at 7.97, while the 11.6μ band appears to be of the Q branch type. The sharp minimum at 14.35μ may perhaps be taken as another Q branch, the corresponding P and R branches being lost in the general background.

Measurements on two Raman plates showed lines at 807, 867, 1123, 1269, 1488, 2914, 2958, and 3007 cm^{-1}. This is in good agreement with recent work of Ananthakrishnan,[4] except that this author finds, in addition, lines at 1159 and 3062 cm^{-1}. The frequencies assumed for the heavy particle vibrations were 807, 869, and 1270 cm^{-1}.

Table II. *Positions of ethylene oxide bands.*

Description	Wave-length (μ)	Frequency (cm^{-1})
	1.61	6211 ± 100
	2.32	4310 ± 70
	2.57	3891 ± 40
	3.31	3021 ± 20
	3.80	2632 ± 20
	4.34	2304 ± 10
	4.94	2024 ± 8
	5.77	1733 ± 6
	6.15	1626 ± 5
	6.70	1493 ± 5
R Branch	7.90	1266 ± 3
Center	7.97	1255 ± 3
P Branch	8.04	1244 ± 3
	8.82	1134 ± 3
R Branch	11.42	875 ± 2
Q "	11.60	862 ± 2
P "	11.80	847 ± 2
	12.43	804 ± 2
	14.35	696 ± 3

In conclusion I wish to express my thanks to Dr. R. Bowling Barnes, formerly of this university, for his advice in connection with these measurements.

[3] Harris, Ashdown and Armstrong, J. Am. Chem. Soc. **58**, 852 (1936).

[4] R. Ananthakrishnan, Proc. Ind. Acad. Sci. **4**, 82 (1936).

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Chemical Applications of the Raman Effect: I. Polymerization

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The Raman spectra of methyl methacrylate and similar compounds have been investigated and interpreted. The changes in the molecular constitution on polymerization indicate the disappearance of a linkage and the like disappearance of the C=C linkage. Lower frequencies appear indicating an increased chain length and a slight decrease in the complexity of the intermediate frequency would seem to indicate an increase in the symmetry of the molecule. The force constants of the more characteristic groups are closer to the *cis-* than the *trans*-modification of the isomer. Unlike inorganic glasses, the polymer exhibits at least some sharp lines. These permit an explanation of the continuing structure present throughout the solid and the mechanism by which this structure comes into existence.

THE Raman spectra of methyl methacrylate as the monomer and in different stages of polymerization were investigated in order to obtain some information concerning the mechanism of polymerization and the molecular constitution of an amorphous compound having the

properties of a glass. In addition, two other compounds, ethyl maleate and ethyl fumarate, were studied and their spectra compared with those obtained from the methyl methacrylates. The results indicate noticeable constitutional changes on polymerization and the existence of a coupling mechanism by direct addition on the ethylenic double-bond.

The polymerization of styrene to polystyrene was investigated by Signer and Weiler[1] by means of the Raman effect. Notwithstanding the complex constitution of the polymer this yielded strong evidence of the polymerization through the ethylenic group. The relative simplicity of the methyl methacrylate polymer provides a more suitable material for a study of the mechanism of a polymerization process and the constitutional changes occurring on the formation of an amorphous glass-like compound.

Most inorganic glasses yield spectral lines which are broad and diffused and are not readily correlated with those of the crystalline material from which they may be derived. The methyl methacrylate glass yields a spectrum slightly more diffused than that of the liquid, but the lines are well defined and the changes in interatomic binding on polymerization are easily discernible.

The results are presented in Table I together with the data of Dadieu, Pongratz and Kohlrausch[2] for methyl crotonate and methyl isocrotonate. Liquid methyl methacrylate and the two crotonates are isomeric with each other, the isocrotonate representing the *cis*- and methyl crotonate the *trans*-modification.[3] Diethyl maleate bears a like relation to the fumarate. These compounds differ from the crotonates in the substitution of a $COOC_2H_5$ group in place of the methyl radical and because they are the ethyl instead of the methyl esters.

In comparing the spectra from these diethyl derivatives it is to be noted first that the frequency shift corresponding to the C=C linkage is influenced much more by *cis-trans*-isomerism than by any other factor, the *trans*-modification having a value between 11 and 15 wave numbers higher than the corresponding *cis*-compound. Dadieu, Pongratz and Kohlrausch[2] and Ffolliott[4] have indicated a doubling of this frequency for the diethyl fumarate into two frequencies, $\Delta\tilde{\nu}$ 1640 and 1657. A microphotometer tracing of these spectra indicates no such splitting of this frequency. This is shown in Fig. 1, tracing 1

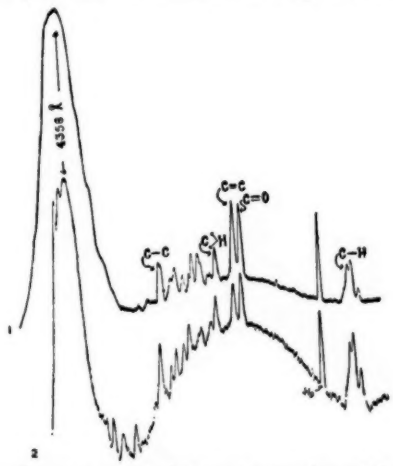


FIG. 1. Curve 1, microphotometer tracing of the Raman spectrum of diethyl fumarate; curve 2, of diethyl maleate.

representing diethyl fumarate and tracing 2, diethyl maleate. Furthermore, the first-mentioned authors gave a value for the diethyl maleate (*cis*) of $\Delta\tilde{\nu}$ 1653 instead of 1641 as observed by the writer, which is an augmented value for this frequency which is inconsistent with the frequencies observed from many other compounds of the type R−CH=CHR which exist in two geometric modifications. This is further confirmed by the comparable shifts reported for methyl isocrotonate (*cis*) $\Delta\tilde{\nu}$ 1644 and methyl crotonate (*trans*) 1655. Other differences between the observations of the writer and the other investigators lie primarily in the group of frequencies noted between $\Delta\tilde{\nu}$ 354 and 748 and the shifts at $\Delta\tilde{\nu}$ 982 and 1402 in the fumarates, and in the further fact that no frequency was observed at $\Delta\tilde{\nu}$ 1840 as previously reported. It may also be pointed out here that while the two crotonates have many shifts in common with each other there is very little general similarity between either of these isomers and methyl methacrylate.

The C=C shift occurring in methyl methacrylate monomer[5] and polymer presents an inter-

[1] Signer and Weiler, Helv. Chim. Acta **15**, 649 (1932).
[2] Dadieu, Pongratz and Kohlrausch, Monatsh. **60**, 205 (1932).
[3] K. v. Auwers and H. Wissebach, Ber. **56**, 715 (1923).
[4] Ffolliott, Phys. Rev. **36**, 367 (1930).
[5] The writer is indebted to H. F. Meindl of the E. I. duPont Company for samples of the monomer. The polymer was prepared from the monomer by irradiation.

esting contrast to the compounds just discussed and provides direct evidence regarding the mechanism of the polymerization process. The frequency is $\Delta\tilde{\nu}$ 1638 in the monomer and in the polymerized product it is completely absent. This is indicated in Fig. 2, which shows three stages of polymerization, curves 1, 2 and 3, representing the monomer, partial polymerization and complete polymerization respectively. In other words, the absence of an ethylenic shift for the polymer is strong evidence of a coupling of the molecules on polymerization by the breaking of the C=C double-bond. This would tend to create chain aggregates, each of much longer dimensions than the original monomer. Such an increase in chain length would naturally be reflected in a change in the C−C vibrations. This is demonstrated by the appearance of a frequency at $\Delta\tilde{\nu}$ 974 which possibly represents an accidental degeneracy of the two frequencies, $\Delta\tilde{\nu}$ 940 and 1008, and would indicate, consequently, an increase in symmetry of the molecule. Appearance of other lines at very low shifts is also indicative of an increase in chain length. The frequencies occurring between $\Delta\tilde{\nu}$ 1100 and 1300 in all the other compounds are apparently absent in either the normal methyl methacrylate or its polymer.

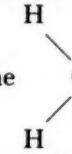
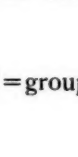
Considering next the carbonyl frequency, it is observable that it appears in the methacrylates in a position intermediate between the values found for this displacement in crotonates and the two dicarboxylic esters. It is somewhat lower than its normal value in saturated esters, namely $\Delta\tilde{\nu}$ 1736. This would ordinarily be attributed to conjugation with the ethylenic group but there

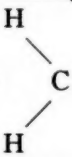
TABLE I. *Raman spectra of some unsaturated isomers.*

Methyl Metha-crylate (Liquid)	Methyl Methacrylate (Solid)	Methyl Crotonate	Methyl Isocrotonate	Diethyl Maleate	Diethyl Fumarate
$\Delta\tilde{\nu}$ i	$\Delta\tilde{\nu}$ i	$\Delta\tilde{\nu}$ i	$\Delta\tilde{\nu}$ i	$\Delta\tilde{\nu}$ i	$\Delta\tilde{\nu}$ i
—	—	—	—	—	179(2)
—	—	210($\frac{1}{2}$)	—	—	255(2)
—	299(1)	—	—	—	—
—	—	336($\frac{1}{2}$)	—	—	354(0, *d*)
377(3)	367(2, *b*)	387(5)	358(3,*b*)	389(2)	388(0, *d*)
—	487(2, *b*, *d*)	450(1)	—	478(1, *b*)	—
507(2)	—	495(1)	521(3)	—	—
599(2)	599(3)	—	—	600(2)	648(0, *d*)
656(0)	—	723(2)	734(3)	—	—
—	806(6)	—	—	795(0)	748(1, *d*)
835(6)	—	844(3)	—	—	—
—	—	—	890(5)	869(6)	865(6)
—	—	905(1)	—	—	894(6)
940(2)	—	935(1)	—	—	—
—	974(5, *b*, *d*)	986($\frac{1}{2}$)	—	977(2)	982(0)
1008(2)	—	—	1013(2)	—	—
—	—	1044(2)	1040(2)	1028(3)	1032(3)
—	1116(1)	1107(2)	—	1115(1)	1111(3)
—	—	1183(3)	1192(2)	1167(3)	1169(1)
—	—	1201($\frac{1}{2}$)	—	—	1216(4)
—	—	—	1245(3)	—	1269(4)
—	—	1293(4)	—	1287(1, *d*)	1304(2)
1332(1)	1335(0, *b*)	—	—	—	—
—	—	1375(4)	1367(2)	—	1371(1)(?)
1404(5)	—	—	—	1397(1, *d*)	1402(1)
1451(3)	1448(*b*, *b*)	1444(5, *b*)	1444(4, *b*)	1453(5)	1457(5)
1638(8)	—	1655(8)	1644(10)	1641(7)	1656(9)
1722(7)	1725(3)	1715(2)	1715(5, *b*)	1730(8)	1725(8)
2855(0)	2855(0)	2856($\frac{1}{2}$, *b*)	—	—	—
2937(3)	—	2917(5)	2920(3, *b*)	2934(4)	2935(4)
—	2947(2)	2950(4)	2950(3, *b*)	—	—
—	—	—	—	2993(6)	2985(6)
3005(1)	3005(1)	3031(3)	3046(2)	—	—
—	—	—	—	3060(3)	3060(3)
3100(3)	—	—	—	—	—

$\Delta\tilde{\nu}$ = wave numbers per centimeter.
i = relative intensity on basis of ten.
b = broad.
d = diffuse.

is no marked increase on polymerization. From the relative intensities of the shifts corresponding to the C=O and C=C groups, respectively, it is noticeable that in the *trans*-modifications the intensity of the line originating in the C=O group is weaker than the C=C line. On the other hand, in the *cis*-modifications the relative intensity of the C=C line may not be so much greater than the C=O one or, as in diethyl maleate, even less intense. Methyl methacrylate, therefore, more closely resembles the *cis*-compounds than the *trans*- so far as this relationship is concerned.

It has already been mentioned that the disappearance of the ethylenic double bond in the solid methyl methacrylate was evidence for a continuous chain system propagated by means of additions to the  grouping. If this is the case then there should also be characteristic modifications in the C↔H vibrations of the original  grouping. This apparently takes place.

There is an appearance of a relatively strong frequency at $\Delta\tilde{\nu}$ 1404 which presumably is similar to that at $\Delta\tilde{\nu}$ 1450 which in turn is connected with the transverse vibration of a hydrogen atom. However, it is virtually missing in the other compounds cited in Table I and consequently $\Delta\tilde{\nu}$ 1404 probably is connected more specifically with the transverse vibration of the hydrogens directly attached to the carbon atom bound by an ethylenic linkage. Increasing the chain length by polymerization through this linkage results in a removal of the  grouping and the consequent disappearance of the frequency at $\Delta\tilde{\nu}$ 1404.

If organic compounds containing nitrogen, furanes, epoxy compounds, cyclopropanes and acetylenes are omitted from consideration as not being pertinent to the discussion, the only hydrocarbons exhibiting a frequency greater than $\Delta\tilde{\nu}$ 3000, corresponding to a linear oscillation of a hydrogen atom against a carbon atom, are most of those compounds containing the C=C grouping. The aromatic hydrocarbons and most

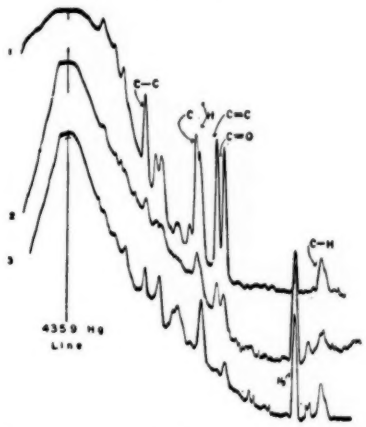
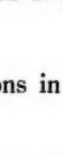


FIG. 2. Curve 1, microphotometer tracing of the Raman spectrum of liquid methyl methacrylate; curve 2, of partially polymerized methyl methacrylate; curve 3, of solid or completely polymerized methyl methacrylate.

of the cycloölefins give rise to a shift near $\Delta\tilde{\nu}$ 3060 for the C–H group. In all unsaturated hydrocarbons containing the double bond in the 1-position ($RC=CH_2$) there are two characteristic frequencies, $\Delta\tilde{\nu}$ 3005 and 3060–3080, for this type of linkage.[6] Other compounds such as limonene and carvone which possess external double bonds of the type $-C=CH_2$ yield frequencies in the region of $\Delta\tilde{\nu}$ 3080 but pulegone with the external group of $-C=C(CH_3)_2$ has a maximum frequency of $\Delta\tilde{\nu}$ 2951. Diethyl maleate and fumarate having the general formula RCH=CHR yield $\Delta\tilde{\nu}$ 3060, the lower shifts near 2990 and 2935 being ascribed to the hydrogen vibrations in the  and CH_3 groups. The effect of substituting a negative group for a hydrogen radical in compounds of the type $RCH=CH_2$ is to augment the hydrogen frequency from an average value of $\Delta\tilde{\nu}$ 3080 to a higher one, as for example, in acrylic acid and vinyl chloride the shifts are $\Delta\tilde{\nu}$ 3111 and 3134, respectively.

[6] Hibben, Chem. Rev. **18**, 1 (1936).

In view of these facts, therefore, it is not surprising that methyl methacrylate monomer possesses a frequency at $\Delta\tilde{\nu}$ 3100 corresponding to the linear oscillation of the hydrogen atoms attached to the ethylenic group and an additional frequency at $\Delta\tilde{\nu}$ 3005, likewise attributable to the movement of hydrogen atoms. In the completely polymerized product, on the other hand, the large shift at $\Delta\tilde{\nu}$ 3100 is completely absent. The only reasonable explanation of this disappearance is found in the absence of the $=CH_2$ group. This is additional evidence of the breakdown of the ethylenic linkage and the formation of a chain through the end carbon atom.

Up to this point little has been said in regard to the spectrum shown in Fig. 2 for partially polymerized methyl methacrylate. This spectrum, as is apparent, is practically identical with that of the unpolymerized monomer. The solutions in these experiments with the partially polymerized product were varied over a wide range of viscosities from a value approximating that of glycerine to a solution so highly viscous that no flow was observed in a period of 24 hours under a pressure corresponding to several centimeters of the liquid. The actual viscosity is of little importance. The essential fact is that, after increasing the viscosity until it has reached a value many thousand times its initial amount the spectrum remains largely unchanged. These observations are susceptible of but one interpretation. A small amount of polymerization has an enormous effect on the viscosity. Any concentration of the polymer in excess of 5 percent to 10 percent would have been detectable. In the absence of such indication, less than this amount of polymerization must produce the marked alteration in physical properties.

The microphotometer used to trace the photographic plates is a two-speed Kipp and Zonen type A Moll instrument. The spectrograph used in these experiments is the Gaertner model L 230 having a single glass prism with a camera lens having an effective aperture of F 16. The dispersion on the photographic plates at λ4358 was 35A per millimeter. The wave-lengths of the Raman lines were determined by interpolation from the nearest iron arc lines.

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Chemical Applications of the Raman Effect: II. Common Ion Effect

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It has been shown by means of the Raman effect that the ionization of homopolar compounds in dilute solution increases more rapidly than is proportional to the dilution. This ionization will be repressed by adding a common ion and such repression is proportional to the concentration of the common ion added. In mixtures of two compounds, both being homopolar and containing a common cation, there is little effect on the ionization. On the addition of a neutral salt containing an anion which may be shared with a cation already combined in homopolar linkage with another anion the equilibrium resulting is in the direction of the formation of that compound whose linkage is the most homopolar. These results indicated by means of the Raman effect cannot be observed with equal facility by any other method of approach.

THE influence of adding common ions to solutions of compounds whose anions are bound by a linkage homopolar in nature is investigated by means of the Raman effect. This is possibly the only practical method for investigating solutions of this type. While the results are in more or less agreement with what may be expected from the classical theory of the common ion effect, there has heretofore been no extensive means available which would permit such a correlation.

The Raman spectra of aqueous solutions of zinc chloride and its combinations with alcohol have been previously investigated by Hibben.[1,2]

[1] Hibben, Proc. Nat. Acad. Sci. **18**, 532 (1932).
[2] Hibben, Phys. Rev. **51**, 593 (1937).

The aqueous solution gives rise to at least one line corresponding to the Zn↔Cl (ν_π) oscillation of 275 wave numbers per centimeter. In concentrated solutions its intensity indicates a strong homopolar linkage. In the more dilute solutions there is a diminution of the intensity with increased ionization. Consequently any suppression of ionization will increase the intensity of this line as Zn^{++} and Cl^- are incapable of giving rise to any Raman effect.

From the classical theory of the common ion effect, the addition of the Cl ions should be in the direction of repressing ionization and consequently increasing the intensity of the Raman line corresponding to the Zn↔Cl vibration. However, such observations as have been made heretofore were either on dilute solutions or solutions in equilibrium with two phases. These experiments indicate that there is a repression of ionization on the addition of a common ion in both dilute and concentrated solutions, even though the solution may be apparently homogeneous, and in the complete absence of a two-phase equilibrium. In addition to these effects there is indicated, in the case of zinc chloride solutions, a greater increase in ionization on dilution than is proportional to the amount of dilution. These results are indicated in Fig. 1.

Beginning with a 1 molal zinc chloride solution the concentration is decreased to one-half, at which point, as is illustrated in curve 2, the intensity of the Zn−Cl shift is not diminished to one-half but to nearly zero, which indicates that in a half molal $ZnCl_2$ solution there is practically complete ionization. But on the contrary in a solution of a $\frac{1}{4}$ molal zinc chloride and 1 molal sodium chloride, there is some evidence for the reappearance of the Zn−Cl shift. Keeping the zinc chloride concentration to $\frac{1}{4}$ molal, but increasing the sodium chloride to 2 molal, enhances the intensity of the Zn−Cl line so that it is nearly one-half the value noted in the original 1 molal solution of zinc chloride. With $\frac{1}{2}$ molal zinc chloride solution, 2 molal with respect to sodium chloride, the intensity is even greater than with the 1 molal solution. This would indicate that the 1 molal solution of zinc chloride was at least 50 percent ionized, and that such ionization will be increased with the dilution to an exceptional degree. This may be repressed by the addition of the common chlorine ion, such repression being roughly proportional to the concentration of such an ion. There seems to be, however, a minimum effectivity since the production of free chlorine ions from the ionization

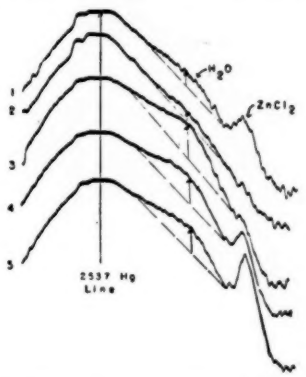

FIG. 1. Microphotometer tracings of the Raman spectra from zinc chloride solutions of the following compositions: curve 1, 1 molal zinc chloride; curve 2, ½ molal zinc chloride; curve 3, ¼ molal zinc chloride 1 molal sodium chloride; curve 4, ¼ molal zinc chloride 2 molal sodium chloride; curve 5, ½ molal zinc chloride 2 molal sodium chloride.

of the zinc chloride alone in passing from 1 molal to $\frac{1}{2}$ molal solution is insufficient to accomplish this effect.

In these solutions there is also a concomitant effect upon the water band occurring near $\Delta\tilde{\nu}$ 150–170 attributed to the hindered translational motion of the water molecules. This is apparently enhanced by the sodium chloride and is diminished by small quantities of zinc chloride.

The next logical procedure would be to ascertain the effect of adding a common zinc ion. For this purpose zinc sulfate was chosen. This gives rise to at least four frequencies, $\Delta\tilde{\nu}$ 448, 614, 980 and 1105. These are in reasonable agreement with similar frequencies observed in other sulfates. There is some evidence of a frequency slightly less than $\Delta\tilde{\nu}$ 448 which is broad and diffuse. These results are shown in Fig. 2, in which curve 1 represents a 1 molal solution of zinc sulfate, and curve 2, a 1 molal zinc chloride solution. The line occurring in close proximity to $\Delta\tilde{\nu}$ 614 is the 2576A mercury line. Curve 3 represents 1 molal zinc sulfate and 1 molal zinc chloride solution from which it is observed that neither the Zn−Cl line nor the SO_4 lines are appreciably affected either in intensity or in magnitude of displacement. Curve 4 represents a mixture, the

solution originally having the composition sodium chloride, 4 molal, and zinc sulfate, 2 molal. Finally curve 5 is for a 2 molal sodium chloride and ½ molal zinc chloride solution. From

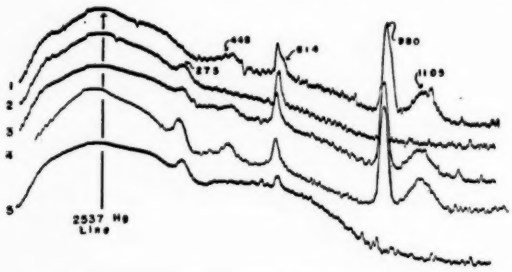

FIG. 2. Microphotometer tracings of the Raman spectra from zinc chloride and zinc sulfate solutions of the following compositions: curve 1, 1 molal zinc sulfate; curve 2, 1 molal zinc chloride; curve 3, 1 molal zinc sulfate 1 molal zinc chloride; curve 4, 4 molal sodium chloride 2 molal zinc sulfate; curve 5, ½ molal zinc chloride 2 molal sodium chloride.

these last two curves it is apparent first that the sodium chloride reacts with some of the zinc sulfate to form zinc chloride but not with all of it. In other words, if the equilibrium were entirely in the direction of formation of zinc chloride and production of sodium sulfate, the line at $\Delta\tilde{\nu}$ 275 in curve 4 should have at least twice the intensity it has in curve 3 if the degree of ionization in a 1 molal and 2 molal solution does not differ greatly. This is not quite realized. On the other hand, if there were equal interchange of all ions so as to produce a 2 molal sodium chloride and 1 molal zinc chloride solution, omitting the sulfates from consideration, the $\Delta\tilde{\nu}$ 275 line in curve 4 should have approximately twice the intensity it has in curve 5. This also is not realized. Consequently one is led to the conclusion that the equilibrium in such mixtures is slightly in the direction toward the formation of excess zinc chloride. However, in view of the amount of experimental error involved in treating these curves from a strictly quantitative point of view, such a deduction can be considered as only tentative. From curve 3 can be drawn the conclusion that the effect of the zinc ion is not to repress noticeably the ionization of zinc chloride, but to leave the equilibrium relatively undisturbed. This is possibly due to the equal homopolarity of the bonds in either case.

The spectrograph used in these experiments was designed by the author. The optical system consists of two quartz lenses, focal length 24 centimeters, effective aperture F 6.5, each fully corrected for spherical aberration, and one right-hand and one left-hand 60° quartz prism. The dispersion on the photographic plates at λ2537 is 16.5A per millimeter. The microphotometer used to trace the plates is a two-speed Kipp and Zonen type A Moll instrument. The wavelengths of the Raman lines were determined by interpolation from the nearest iron arc lines. The source of excitation was a special model of the Hanovia Sc 2537 silica lamp.

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Some Chemical Properties of Element 43

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1. INTRODUCTION

PROFESSOR E. O. LAWRENCE gave us a piece of molybdenum plate which had been bombarded for some months by a strong deuteron beam in the Berkeley cyclotron. The molybdenum has been also irradiated with secondary neutrons which are always generated by the cyclotron. The molybdenum plate shows a strong activity, chiefly due to very slow electrons. The radioactivity is due to more than one substance of a half-value period of some months and to the radioactive phosphorus isotope P^{32}.[1] The substance was sent from Berkeley on December 17, 1936 and we started our chemical investigation on January 30, 1937; all short period substances have decayed in these 6 weeks and we could

[1] We will give more details on the radioactive side of this investigation in a later paper to appear in the *Physical Review*.

investigate only substances with a comparatively long period.

According to usual nuclear reactions one would expect to find in molybdenum irradiated with neutrons or deuterons the formation of isotopes of zirconium, columbium, molybdenum, and element 43, of which zirconium can be produced only by fast neutrons and element 43 by deuterons, whereas molybdenum and columbium could be formed by deuterons and by neutrons.

There is always, of course, the possibility that the activity is due to some impurity of molybdenum, but we will show that this cannot play any important part in the formation of our radioactive isotopes. However, we found also a strong activity of P^{32}, possibly due to some surface contamination. Initially we did not eliminate this impurity which interfered considerably with the beginning of the analysis. Later on, some precipitates showed the decay period and the absorption coefficient for β-rays characteristic of P^{32} and we checked this result chemically, eliminating any P^{32}. For some reason, which we do not know, it seems that every substance which has been bombarded in the Berkeley cyclotron is strongly contaminated with P^{32}. We have employed the P^{32} extracted from molybdenum and from other metals of the cyclotron's walls as an indicator for some biological experiments.[2] The two faces of the molybdenum plate showed very different activities hence the transmutation is chiefly due to particles which are efficiently stopped by the molybdenum plate i.e. to charged particles (deuterons).

2. Analysis

In a first analysis we tested whether the activity was due to columbium. About 200 mg of molybdenum with an activity of some thousands of our radioactive units (R.U.)[3] were dissolved in aqua regia, and after adding 5 mg of rhenium, evaporated to dryness. The residue was dissolved with potassium hydroxide containing a small amount of potassium columbate. The addition of rhenium and the subsequent addition of manganese were made in order to protect any 43 in the later precipitations. We had no stable isotope of 43 and as very little is known about its chemical properties, we added the elements having presumably the closest resemblance to it. These are manganese and rhenium which lie in the same column of the periodic system above and beneath 43. We will see however that the resemblance with rhenium is much closer than the resemblance with manganese; a result which was expected.[4]

Manganese was added as manganese columbate prepared separately adding a slight excess of potassium columbate to a solution of manganous sulfate and ammonium sulfate. Manganese columbate being little soluble remains suspended in the mixture. Adding this mixture to the molybdenum solution the precipitate showed a tendency to blacken immediately on account of the evident formation of manganese dioxide; a few drops of hydrogen peroxide were added in order to ensure a complete precipitation of manganese; afterwards we passed a current of carbon dioxide through the solution in order to secure a precipitate of columbium pentoxide possibly free from molybdenum.

This precipitate was very active; we fused it with potassium carbonate and nitrate. The fused mass was extracted with water and the solution reduced with alcohol. Repeating this treatment a few times we got a perfectly inactive residue of manganese dioxide.

To the alkaline solution containing columbium we added sulfuric acid and precipitated columbium pentoxide. We added 7 mg of ammonium sodium phosphate and 20 mg of zirconium nitrate to the acid solution. The precipitate contains columbium, phosphorus and zirconium; it is very active (more than 1000 R.U.). We fused it repeatedly with potassium carbonate and potassium hydrate; each time we extracted the fused mass with water and acidified the solution with sulfuric acid in order to isolate columbium. However, we obtained always precipitates showing a definite activity, though the activity did not follow quantitatively columbium and had the radioactive characters of P^{32}. Finally we took a rather large quantity of columbium pentoxide which showed an activity of 56 R.U. and starting from it we prepared crystalline sodium metacolumbate. The identity of this salt was checked also by its optical and crystalline

[2] Nature (London) **139**, 836 (1937); ibid. in press.

[3] The β-activity of 1 gram of uranium corresponds to about 300 R.U.

[4] See e.g. I. and W. Noddack, Naturwiss. **6**, 333 (1927).

characters; it showed no activity and we could precipitate quantitatively the activity from the solution as magnesium ammonium phosphate whose identity was also checked crystallographically. We may conclude from these tests that columbium does not have any activity.

Subsequently we found that also fractions containing zirconium were inactive. We dissolved some active molybdenum in aqua regia, added 7.5 mg of rhenium, 10 mg of zirconium nitrate and evaporated over the water bath. We transformed the molybdic acid into ammonium molybdate by adding a little ammonia; and we added afterwards an excess of nitric acid. We obtained a precipitate of ammonium phosphomolybdate and zirconium phosphate which showed a strong activity. We treated this precipitate with ammonia but the activity did not change appreciably, indicating that only a small fraction of phosphorus had been converted into ammonium phosphomolybdate; however, this fraction was recovered as magnesium ammonium phosphate. The residue of the first ammonia treatment contained the bulk of phosphorus and zirconium and had an activity of about 1500 R.U. We fused it with sodium carbonate, extracted the fused mass with water, fused again the residue containing zirconium with sodium pyrosulphate and precipitated zirconium hydroxide with ammonia. The precipitate of zirconium hydrate is inactive whereas we recovered quantitatively the activity in this filtrate by precipitating phosphorus as magnesium ammonium phosphate. This test rules out the presence of a radioactive isotope of zirconium.

We were able to show that molybdenum also cannot be responsible for the activity. Of several tests we mention only the following. Rhenium and phosphorus and ammonium nitrate were added to the molybdenum solution. Ammonium phosphomolybdate precipitated; we dissolved it with ammonia and separate phosphorus as magnesium ammonium phosphate and molybdenum as sulphide. The former carries every activity, whereas molybdenum sulphide is inactive.

We have thus shown that the activity is not due to columbium, zirconium, or molybdenum. On the other hand the radioactivity of the irradiated molybdenum has radioactive characters quite different from P^{32} which was the only radioactive substance found until this point of the research. We had to investigate, as already pointed out, the possible presence of a radioactive isotope of the element 43 (masurium of I. and W. Noddack).[5] This should be found in the fraction containing rhenium since we did not find any trace of activity together with manganese.

Since from the first analysis we had an indication that the activity could be contained in a rather volatile substance as one would expect the higher oxides of 43 to be. We had precipitated the sulphides in an acid solution after separation of columbium. The precipitate showed an activity which was reduced to less than one-half of its former value by a very moderate ignition.

However, due to the absence of a stable isotope of element 43 and to the extreme scarcity and uncertainty of information about its chemical properties, it seemed worth while to investigate further the chemical properties of the activity in order to obtain some chemical information about element 43 and to obtain the chemical characteristics of the carrier of the activity.

A considerable difficulty in this investigation comes from the extreme softness of the emitted radiation, whose half-value thickness is about 1.5 mg/cm^2; moreover, the absorption curve is far from exponential and it is practically impossible to correct properly the measured activity values in order to take into account the absorption of the β-rays from the precipitates. This difficulty is even increased for some fine precipitates (e.g., sulphides) which penetrate into the pores of filter paper, and show, for this reason, a smaller activity than they really have. Until now we have not secured a better filtering device.

3. Chemical Properties of Element 43

The first step for any chemical study of the activity is its concentration with the smallest possible amount of inactive substance. The best method for this concentration we have found, is to dissolve about 200 mg of irradiated molybdenum in aqua regia, add from 2 to 5 mg of rhenium and evaporate over the water bath. The residue is then dissolved with ammonia, and hydrogen sulfide passed through the solution.

[5] W. Noddack, I. Tacke, O. Berg, Sitzber. preuss. Akad. Wiss. Physikmath. Klasse, **19**, 400 (1925).

We then add a few milligrams of a manganous salt and after standing 12 hours filter.

The precipitate of manganous sulphide carries a small amount of a black substance, possibly rhenium sulphide or some sulphoperrhenate.[6] This precipitate contains the bulk of the activity. It can be freed completely from manganese with dilute hydrochloric acid and, if necessary, with sulfur dioxide without any loss of activity. To check this last point we precipitated the solution containing the dissolved manganese again with hydrogen sulfide and collected manganese sulphide of the normal pink color, and found it inactive.

The black substance carrying the activity is easily dissolved in cold hydrogen peroxide, as does rhenium sulphide and shows also some other rhenium reactions. However, in order to have a better knowledge of its chemical nature, we repeated the precipitation of manganese with hydrogen sulphide, both from a molybdenum solution without rhenium and from a rhenium solution without molybdenum. The former gave a pink manganese sulphide, and the precipitate was easily and completely dissolved in dilute hydrochloric acid, the latter on the other hand gave a black precipitate with the properties stated above.

Further rhenium additions and manganese precipitations from the same molybdenum solution give the usual black precipitate, but its activity decreases rapidly in successive separations, e.g. Three separations with the method described above, from the same active molybdenum solution yield activities of 1000.20 and 0 R.U. Similar results, but not so clear cut and with a lower yield were obtained also by substituting zinc for manganese.

Another way of concentrating the activity is to heat the active molybdic anhydride, to which some rhenium has been added, in an oxygen current at about 550°. Rhenium volatilizes and carries the activity which may be collected together with rhenium in an alkaline solution and precipitated as sulphide according to Noddack.[4]

The active rhenium sulphide produced by one of the above described methods is dissolved in hydrogen peroxide and the activity measured by evaporating 1 cc of the solution over the water bath on a crucible cover. Solutions standardized in this way contained of an order of magnitude 0.05 mg of rhenium and had an activity of about 20 R.U. per cc. Due to the preparation method it is probable that the elements were in their highest normal oxidation state.

With the titrated solutions mentioned above we have performed the following reactions:

Sulphides

We added hydrochloric acid to the solution and passed hydrogen sulfide through it. The activity was transferred practically quantitatively along with rhenium, copper, and cadmium. The hydrochloric acid concentrations were, respectively, 12 percent, 4 percent and 1 percent of hydrochloric acid.

Rhenium sulphide was treated with yellow ammonium sulphide without any loss of activity. The active product on the other hand is easily dissolved, as stated above, with hydrogen peroxide together with rhenium sulphide.

Oxidation and reduction

According to the position of element 43 in the periodic table, one would expect oxidation and reduction reactions to have a considerable importance for the chemistry of this element. The only data we could collect until now are the following: we add to the active solution a manganese salt and precipitate manganese dioxide with nitric acid and potassium chlorate. The precipitate is not active. We add potassium permanganate to an alkaline active solution and we reduce manganese with alcohol; no activity is found in the manganese dioxide precipitate. We add potassium ruthenate to the active solution, and precipitate ruthenium by reduction with formaldehyde. No activity is found in the precipitate. On the other hand metallic zinc precipitates the activity from a hydrochloric acid solution with a good yield.

Volatility

According to the position of element 43 in the periodic table one expects the higher oxides to be rather volatile. A first indication of this point was given, as we said, by the first analysis. Since volatility is analytically important, we have investigated it more carefully. It depends of course upon the valency of the investigated

[6] W. Feit, quoted by I. and W. Noddack, *Das Rhenium* (Leipzig 1933), p. 57.

compounds. We have tried to reach the highest oxidation.

In a series of tests we have evaporated a few cc of the active solution on porcelain crucible covers over the water bath and measured the activity of the residue. Evaporation over the water bath, even if repeated, does not diminish the activity. Heating the covers to 400° causes the activity to begin to decrease and at 500° it disappears rapidly. In these experiments we have tried to evaporate acid anhydrydes without alkali. However, we do not know whether we have done this since the residue contains a small fraction of a milligram of rhenium and even a trace of a base would be sufficient to neutralize the anhydryde. As a check we have volatilized the same solution after alkali addition. The volatilization temperature was only slightly higher.

As it is well known[7] rhenium may be separated quantitatively from molybdenum by passing moist hydrochloric acid through a strong (80 percent sulphuric acid) sulphuric solution at about 200°. We tried whether under these conditions the activity followed the rhenium or remained in the residue and found that it remains in the residue, e.g., in an experiment we distilled a sulphuric solution containing 200 R.U. of our activity, 5 mg rhenium and traces of impurities, possibly molybdenum, at 180° for one and one-half hours passing moist hydrochloric acid through the solution; 125 cc of the liquid distilled over. We precipitated all the rhenium and a trace of the activity from the distillate with hydrogen sulfide. The greater part of the activity is precipitated from the residue together with a small quantity of impurities by hydrogen sulfide. The activity is then completely recovered by adding a few mg of rhenium to the residue after the first precipitation and precipitating again with hydrogen sulfide. This separation from rhenium is especially important since it is the only method available for separating the activity from rhenium.

We have also separated the activity from a potassium ruthenate solution with a distillation in a chlorine current according to Debray and Joly.[8] Ruthenium distills and the activity remains in the residue. This separation from ruthenium gives information about the volatility in a chlorine current of element 43 and rules out the possibility that the activity is due to ruthenium confirming thus the test referred under "oxidation and reduction."

We have already pointed out that ignition in an oxygen current may be used for separating the activity from molybdenum, though the sulphide method seems to us to be preferred.

Organic reagents

Among the various organic reagents which we have tested, we have had good results in separating the activity from molybdenum with 8-hydroxyquinoline and nitron as Geilmann and Weibke[9] did for the separation of rhenium from molybdenum. Moreover we could also precipitate the bulk of molybdenum with benzidine in presence of rhenium and extract the activity from the filtrate as a sulphide. However, this method of separation is less reliable than the former.

Precipitation of thallium perrhenate according to Krauss and Steinfeld[10] from an active solution carries the largest part of the activity.

Summary

Deuteron irradiated molybdenum shows an activity which has to be ascribed to element 43 according to its chemical characters, since, as is easily seen, all other possible elements are ruled out.

Element 43 in its chemical behavior bears a close resemblance to rhenium showing the same reactions but for the volatilization in a hydrochloric acid current. However, it must be borne in mind that having used rhenium as a "carrier" for extremely small quantities of element 43, some reactions could be different for "weighable" quantities of this element.

Our warmest thanks are due to Professor E. O. Lawrence and to the Radiation Laboratory of the University of California whose most generous gift of radioactive substance made this investigation possible. We hope also that this research carried on months after the end of the irradiation and many thousands of miles away from the cyclotron may help to show the tremendous possibilities of this instrument.

[7] Geilmann and Weibke, Zeits. f. allgem. anorg. Chemie **199**, 120 (1931).

[8] Debray and Joly, Comptes rendus, Paris **106**, 328 (1888).

[9] Geilmann and Weibke, Zeits. f. anorg. allgem. Chemie **199**, 347 (1931).

[10] Krauss and Steinfeld, Zeits. f. anorg. allgem. Chemie **197**, 52 (1931).

Fourier Analysis of X-Ray Scattering from Polyatomic Liquids

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It is shown that the Fourier integral analysis of x-ray scattering for liquids with polyatomic molecules containing like atoms may be simplified if the x-ray diffraction curve is corrected by subtraction of the gas scattering of the single molecules before the analysis is made. The method is tested by an analysis of Katzoff's data for benzene. The distribution function obtained indicates that a given molecule is surrounded by six neighbors in the plane of the benzene ring, with a mean separation of centers of about 6.7A. The neighbors of a given molecule are oriented with respect to the molecule. The parallel planes of flat molecules are separated by a distance of 3.7A. The structure is very similar to the crystal structure of hexamethyl benzene.

THE atomic distribution in a liquid may be determined from x-ray diffraction data[1] by application of the Zernike-Prins equation, which may be written in the form

$$q(r)=\frac{2r}{\pi}\int_0^\infty \frac{k(I-NTf^2)}{NTf^2}\sin kr\,dk, \qquad (1)$$

where $q(r)$ is a radial distribution function giving the excess number of atoms over the average at distance r. (The average number of atoms at distance r is given by the value of $4\pi r^2\rho$, where ρ is the number of atoms in unit volume.) k is the function, $4\pi/\lambda \sin\theta$, where λ is the wave-length and θ is one-half the angle between direct beam and scattered beam. I is the observed intensity, corrected for polarization and for modified radiation. N is the number of irradiated atoms, and T the Thompson scattering per free electron. f is the atomic structure factor.

Two difficulties are encountered in the application[2] of Eq. (1) to the scattering obtained from a liquid containing polyatomic molecules:

1. In order to correct for modified radiation and to express the intensity in the same units as f^2, it is necessary to assume that the atoms scatter independently at large angles. Because of the gas scattering of single molecules this assumption is not valid, for at the largest angles attainable the scattering curve shows maxima and minima[3] due to interference in radiation from atoms within the same molecule. When Eq. (1) is used it is necessary to select arbitrarily a point at which independent scattering is assumed.

2. Because of the gas scattering, the curve $k(I-NTf^2)/NTf^2$ does not damp to zero amplitude in the experimentally attainable region, and it is impossible to perform the integration over the limits of zero to infinity.

These difficulties may both be eliminated if the observed intensity curve is corrected by subtracting from it the gas scattering of the single molecules. This operation gives a hypothetical scattering curve which would be obtained if there were no interference due to atoms within the same molecule. Use of a modified scattering curve necessitates the following revision of the method for calculating the distribution function:

If the Debye equation for the scattering of atoms at fixed distances is applied to a polymolecular system the summation may be made in two operations, one over the atoms in the single molecule, the other over atoms in neighboring molecules. In a system of N molecules, each containing m like atoms, the intensity is given by the relation

$$I=T\sum_1^{mN}\sum_1^{mN} f_if_j\frac{\sin kr_{ij}}{kr_{ij}}=NT\sum_1^{m}\sum_1^{m} f_if_j\frac{\sin kr_{ij}}{kr_{ij}}$$
gas scattering
$$+m(N-1)T\sum_{m+1}^{mN} f_if_j\frac{\sin kr_N}{kr_N}$$
liquid scattering

where r_N is the distance from a given atom to an

[1] F. Zernike and J. A. Prins, Zeits. f. Physik **41**, 184 (1927); P. Debye and H. Menke, Physik. Zeits. **31**, 797 (1930); B. E. Warren, Phys. Rev. **44**, 969 (1933).
[2] See W. C. Pierce, J. Chem. Phys. **3**, 252 (1935).
[3] In electron diffraction from gases, where the effective wave-length is very short, as many as 10–12 maxima and minima can be observed in the scattering curve. Only the first few of these can be observed in x-ray scattering, because of the longer wave-lengths employed.

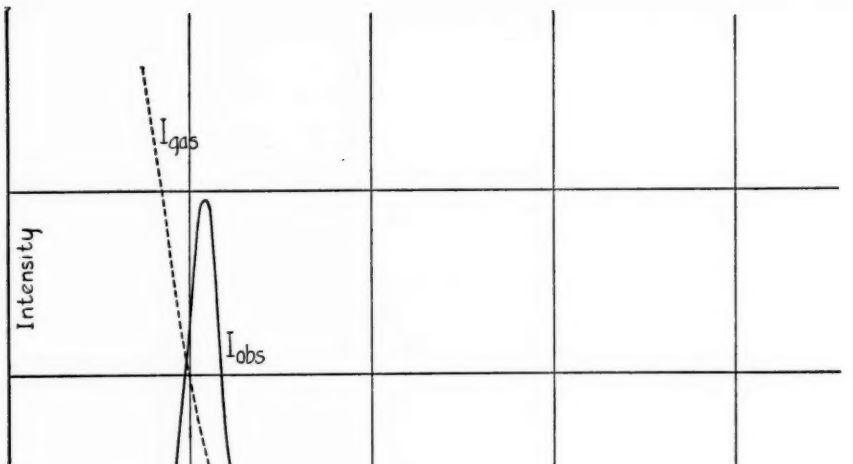

FIG. 1. Method for correcting the experimental scattering curve for the gas scattering of single molecules.

atom in a neighboring molecule. If the atoms are all alike and if every atom has on the average the same surroundings with respect to the atoms of neighboring molecules, the expression reduces to the form

$$I=I_{\text{gas}}+m(N-1)Tf^2\sum_{m+1}^{mN}\frac{\sin kr_N}{kr_N}.$$

As an approximation we may replace $N-1$ by N and replace the single summation over fixed distances by an integral containing the probability function $p'(r)$, which gives the number of atoms in other molecules at radial distance r from a given atom. Then

$$I=I_{\text{gas}}+mNTf^2\int_0^\infty p'(r)dr\frac{\sin kr}{kr}$$

$p'(r)$ may be split into two portions

$$p'(r)=\underset{\text{average}}{4\pi r^2\rho}+\underset{\text{excess}}{q'(r)}.$$

Therefore,

$$\frac{I-I_{\text{gas}}}{mNTf^2}=E'=\int_0^\infty 4\pi r^2\rho dr\frac{\sin kr}{kr}+\int_0^\infty q'(r)dr\frac{\sin kr}{kr}.$$

The first integral is zero except when k is zero, and may be neglected for the finite scattering observed. Therefore

$$E'=\frac{1}{k}\int_0^\infty\frac{q'(r)}{r}\sin kr\,dr.$$

This equation may be solved by the Fourier integral theorem,

$$q'(r)=\frac{2r}{\pi}\int_0^\infty kE' \sin kr\, dr. \qquad (2)$$

Eq. (2) must be considered as an approximation since the assumption is made that each atom has the same number of neighboring atoms, at the same distances. For liquids containing only one kind of atom, in molecules which are relatively far apart, the approximation seems to be justified. The equation may even be applied to scattering by liquids containing two kinds of atoms if they are sufficiently comparable in scattering power, as are carbon and oxygen atoms. It is not, however, applicable to the scattering of such a liquid as carbon tetrachloride, where the atoms are greatly different in scattering power.

In order to test the validity of the suggested modification, the x-ray scattering data of Katzoff for benzene[4] were analyzed. The method for making the corrections is shown in Fig. 1. A gas scattering curve was constructed for coherent radiation, using the structure factor for $C^-(Z=7)$ and neglecting the contribution of the hydrogen atoms. To this was added the incoherent scattering calculated for 6 *CH*, and the combined curve was equated to the experimental curve at a large value of s, by multiplication of the amplitude with a constant factor. It was found that the calculated gas scattering curve approximately fitted the experimental curve at all s values beyond 0.7. By subtraction of the I_{gas} curve from I_{obs}. a curve was obtained for I_{liq}. and this was used for calculation of the distribution function, $q'(r)$. The integration of Eq. (2) was performed graphically for the r values shown in Fig. 2, which gives the distribution function obtained. Since the kE' curve damps to zero at a k value of approximately 4, the integration of Eq. (2) is much more readily performed than that of Eq. (1).

A radial distribution curve was constructed by adding $q'(r)$ values to the average number of atoms at radial distance r. This curve has values of zero up to r distances of about 3.1A, then rises abruptly to the first maximum at about 4.3A. Lack of either positive or negative values at r distances less than 3A supports the belief that the distribution function obtained in the analysis is valid, since if the agreement is fortuitous the combination of density data with x-ray data would probably give an oscillatory curve at values near zero.

The $q'(r)$ curve was used as the basis for construction of a model of the liquid arrangement. A close packing of spherical molecules was rejected, since this leads to a radial distribution widely at variance with the one found. Excellent agreement between model and x-ray distribution functions was found for an arrangement of flat molecules in planes, with the separation of planes about 3.7A. In a plane each molecule is surrounded by six neighbors with an average distance of closest approach about 4.3A. The distance apart of centers is about 6.7A. Molecules in adjacent planes do not lie directly above one another, but in a pyramidal arrangement so that the upper molecule is symmetrically placed with respect to three molecules in the lower plane. This model, which was worked out on the assumption that the average distance of closest approach corresponds to the first peak in the $q'(r)$ curve, is very similar to the crystal structure found for hexamethyl benzene and has the same distance between planes. The postulated planes are not of large extent, but merely refer to the average condition of the molecules surrounding a designated center, and throughout the liquid there will be found a random arrangement of

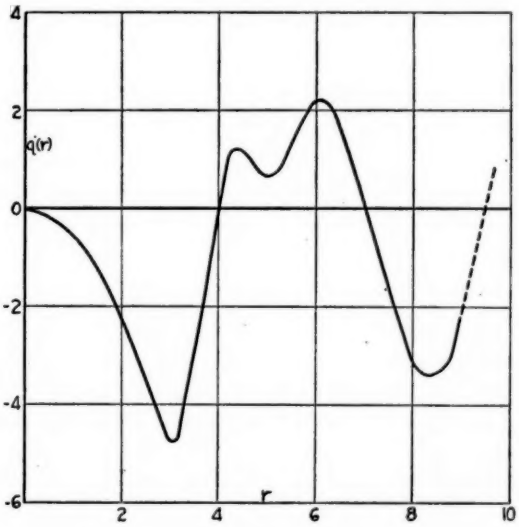

FIG. 2. Distribution function for liquid benzene. $q'(r)$ gives the excess number of atoms, not in the same molecule, at distance r.

[4] S. Katzoff, J. Chem. Phys. **2**, 841 (1934).

planes. Since the atoms do not occupy fixed lattice positions within a plane the Bragg equation cannot be used for calculation of the linear separation of the planes.

The proposed model for the structure in liquid benzene differs from the model employed by Katzoff[4] chiefly in the assumption that the molecules lie flat in planes. Katzoff employed a model based upon crystal structure, in which the molecules lie in planes 3.4A apart and are tilted with respect to the plane. This difference is reflected in the atomic distribution curves obtained in the two cases. Although the $q'(r)$ curve of Fig. 2 qualitatively resembles the distribution curve deduced by Katzoff, the two are not in the same units. Conversion to the same units gives curves which are not in quantitative agreement, although both curves show the double peak observed at 4–7A in Fig. 2. This similarity is due to the assumption employed in both structures that neighboring molecules are oriented within a plane and that upper and lower planes contain molecules likewise oriented. Although the method used here is a little more direct than the one employed by Katzoff the writer does not feel that the resolution obtained in x-ray scattering from a liquid is sufficient to enable one to make definite conclusions as to the uniqueness of either structure.

Katzoff and others have commented upon the bulge at the bottom of the first strong peak in the diffraction pattern (at $s=0.3$). This bulge is also found in the diffraction pattern of benzene derivatives. In the corrected liquid scattering curve of Fig. 1 the bulge becomes relatively more prominent than in the total scattering. It is undoubtedly due, as suggested by Katzoff, to a predominance of interatomic distances of about 4A—a condition which is caused by the orientation of neighboring flat molecules. The absence of this bulge in the diffraction pattern of cyclohexane and of long chain compounds supports this view.

The writer desires to express his appreciation to Professor W. H. Zachariasen for his helpful criticism.

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Calculation of the Rate of Elementary Association Reactions

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An upper limit for the rate of association reactions is found by determining the probability of a decrease of the relative energy of two atoms below zero energy, under the influence of a third body. The relation of this approximate calculation to the rigorous solution of the problem is discussed in Section 2. The results are applied to the recombination of J atoms, measured by Rabinowitch and Wood. Numerically, the agreement is quite good; however, the calculated values are somewhat too low, which cannot be explained by an inaccuracy of the method. Reasons for the discrepancy other than the possible nonadiabatic character of the reaction are discussed.

1

THE transition state method[1] allows the calculation of the rate of reactions which involve an activation energy. The assumptions which one has to make in order to apply this method are (1) that the reaction shall not involve a jump in the quantum state of the electrons,[2] (2) that classical mechanics be applicable to the motion of the nuclei (or that the ordinary way of taking into account quantum effects be justifiable) and, (3) that the number of systems crossing the activated state be the number of systems reacting. This last condition is always satisfied at sufficiently low temperatures and if the energy surfaces are not too complicated, the temperature at which their validity ceases will be rather high.[3] The common feature of the reactions to

[1] Cf. for previous literature e.g. M. G. Evans and M. Polanyi, Trans. Faraday Soc. **31**, 876 (1935).

[2] The possibility of chemical reactions without quantum jumps in the state of the electronic system has been first realized by F. London, *Sommerfeld Festschrift* (S. Hirzel, 1928), p. 104.

[3] Cf. for a closer discussion of these conditions, E. Wigner, Trans. Faraday Soc. (1937).

which the transition state method can be applied in its usual form[4] is that the transition over a state with high energy be the rate determining step.

However, some of the most simple reactions, like the association of atoms to a molecule in a three-body collision, cannot be calculated by the present form of the transition state method, although its original form[5] embraces these reactions also. The purpose of the present note is the derivation of a formula for the rate of reactions of the type $2J+A=J_2+A$, or

$$A_1+A_2+A_3=A_1A_2+A_3. \qquad (1)$$

The assumption of the validity of classical mechanics which will be necessary in the present derivation also, is better fulfilled than for the reactions with activation energy. Also the exact shape of the energy surface enters much less critically, because there is no activation energy Q, and a calculation of the absolute rate is possible at least approximately. On the other hand, there is no limiting case in which the formula (11) to be derived here is a consequence of well-established principles of statistical mechanics. Such a limiting case existed for reactions with activation energy as that of very low temperature and sufficiently heavy masses to assure the validity of classical mechanics.

Eyring, Gershinowitz and Sun[6] have given a very ingenious method by which the rate of (1) can be rigorously calculated if the energy surface can be divided into two regions, both of which are developable. This is very nearly true for that part of the energy surface for the $H+H+H=H_2+H$ reaction which corresponds to the straight configuration of the atoms. However, it cannot be claimed that the majority of associations will proceed from a nearly straight configuration. For a bent configuration, the limits of the integration of Eq. (7) reference 6 should be changed and this will increase the probability of association for bent configurations. Eyring, Gershinowitz and Sun[6] tried to compensate for neglecting to change the limits of their integral by considering the neighborhood of the isosceles triangle configuration also. Thus they counted some reactions twice, some not at all. This criticism of the very ingenious work of reference 6 should not be taken, of course, too seriously, since all that was claimed, and all that can be done at present, is to obtain the reaction rate within a not too large factor. That certainly has been accomplished by Eyring, Gershinowitz and Sun. The point was brought up partly to illustrate the point that an exact calculation of the rate of (1) is not feasible at present[7]—not even under simplifying assumptions for the energy surface—and partly to justify taking up the subject here again.

2

Theoretically,[8] of course, one could obtain the rate of (1) by considering the macrocanonic assembly of systems, containing an A_1, an A_2 and an A_3 atom in a great box of volume v. One can consider then those systems which are in the dissociated state at present but will go over into the right side of (1) within a time t. Whether a point in phase space corresponds to the left or right side of (1), may be ambiguous if all three atoms are close. However, if t is sufficiently large, this ambiguity will extend to a very small proportion of all the systems reacting, most of the molecules formed will be sufficiently far away already from the third body to leave no doubt as to their associated character. On the other hand, t shall not be taken long enough to allow for a second collision, i.e., t shall be small compared with the time between collisions but *very* long compared with the collision time.

The systems which will react before t will be contained in a region R_t of phase space. The ends of this region may be a little uncertain, but the total probability of R_t will be well defined. The

[4] H. Eyring, J. Chem. Phys. **3**, 107 (1935); M. G. Evans and M. Polanyi (reference 1).

[5] M. Polanyi, Zeits. f. Physik **1**, 90 (1920). The first complete outline of the theory has been given in R. Tolman's *Statistical Mechanics* (Chemical Catalog Co., 1927). Cf. also K. F. Herzfeld, *Kinetische Theorie der Wärme* (Müller-Pouillet's *Handbuch der Physik*, second edition, 1925).

[6] H. Eyring, H. Gershinowitz, C. E. Sun, J. Chem. Phys. **3**, 786 (1935).

[7] This does not preclude the possibility of calculating the absolute rate of (1) more accurately than can be done in practice for reactions with activation energy. Although the transition state method should give nearly exact results for the latter, the parameters of the energy surface enter in such a critical way into the formulas that a calculation of the whole rate is hardly feasible at present. Cf. also reference 3.

[8] The second section serves only to establish the connection between the (impracticable) exact calculation of the rate and the approximate calculation of the ensuing sections.

rate constant k is this probability, divided by t.

As we increase t (keeping it still below the time between two three-body collisions), R_t will assume the form of a longer and longer tube in phase space. We can put a surface S across this tube and k will be the number of systems crossing S. It does not matter where the surface S lies, it only must have no wrinkles which could be crossed by the same system twice. All the systems will cross S in the same direction.

The number of decomposing systems can be counted in a similar way. Furthermore, the continuation of S may be taken for the surface for this counting. If we do this, and still allow no wrinkles in S, the number of systems crossing it in one direction will be the number of associations, the number crossing it in the other direction, the number of dissociations (which, naturally, must be equal to the number of associations). Apart from having no "wrinkles," S can be quite arbitrary as long as it divides the whole phase space into two separate parts: those corresponding to the left and the right side of (1). If the distance of A_3 is very great from A_1 and A_2, S must be the $H_0=0$ surface, where H_0 is the mutual energy (potential and kinetic) of A_1 and A_2.

If the distance of the third atom is small, and one still would take $H_0=0$ for S, this S could possibly show wrinkles. These wrinkles would correspond to the relative energy of A_1 and A_2 falling below zero and rising again above this value during the same collision. No association would result then, although, counting the crossings through S in one direction, one would count these crossings. However, one can define an H_0 *depending on all coordinates*, such that $H_0=0$ should have no wrinkles, i.e., no path in phase space shall cross it more than once during one collision. This H_0 will be equal to the relative energy of A_1 and A_2 for great distance of the A_3, will be different from this, however, if A_3 is near to A_1 and A_2. It will divide the whole phase space in two distinct parts and it will have the property that the total number of paths crossing it is as small as possible. This latter condition does not, of course, determine S (and even less H_0), but it determines that minimum number, which is the reaction rate k.

3

We shall calculate now the number of systems crossing the $H_0=0$ surface in unit time. No special assumption concerning the position of this surface will be made in this section and the formulas (3) and (5) hold, therefore, quite generally. In the later sections, however, H_0 will be interpreted (for every position of A_3) as the energy of A_1 and A_2 in the coordinate system in which their center of mass is at rest. Formula (11) will give, therefore, only an approximate value (an upper limit) for the rate constant k.

If H is the total Hamiltonian, we have

$$\begin{aligned}\frac{dH_0}{dt}&=\sum_i\left(\frac{\partial H_0}{\partial q_i}\frac{dq_i}{dt}+\frac{\partial H_0}{\partial p_i}\frac{dp_i}{dt}\right)\\&=\sum_i\left(\frac{\partial H_0}{\partial q_i}\frac{\partial H}{\partial p_i}-\frac{\partial H_0}{\partial p_i}\frac{\partial H}{\partial q_i}\right)\\&=\sum_i\left(\frac{\partial H_0}{\partial q_i}\frac{\partial (H-H_0)}{\partial p_i}-\frac{\partial H_0}{\partial p_i}\frac{\partial (H-H_0)}{\partial q_i}\right).\end{aligned}\tag{2}$$

Those systems will cross the $H_0=0$ surface in the decreasing sense, which are nearer than $(dH_0/dt)/|\text{grad } H_0|$ from it, provided dH_0/dt is negative. We have, therefore (Z is the total integral of $e^{-H/kT}$ over phase space)

$$k=\frac{v^2}{Z}\int\frac{dH_0/dt}{|\text{grad } H_0|}e^{-H/kT}d\sigma,\tag{3}$$

where $d\sigma$ is a surface element of the $H_0=0$ surface and the integration has to be extended over the region in which $dH_0/dt<0$.

This is simply the derivative of the integral

$$I(E)=-\int\cdots\int_{\substack{H_0<E\\ dH_0/dt<0}}(dH_0/dt)e^{-H/kT}\cdot dq_1\cdots dq_n dq_1\cdots dp_n\tag{4}$$

with respect to E at the point $E=0$

$$k=\frac{v^2}{Z}\left(\frac{dI(E)}{dE}\right)_{E=0}.\tag{5}$$

[The real k is (rigorously) the minimum value of this expression for such $H_0(q_1,\cdots,q_n,p_1,\cdots,p_n)$ which go over into the proper energy of the two associating particles for a large distance of the

third body but are not everywhere necessarily equal to it.] The integral $I(E)$ is to be extended over that region of phase space in which $H_0<E$ and also (2) is negative.

4

As an example, the rate of a simple reaction (1) shall be calculated where all A are atoms. The approximate H_0 which shall be used will be (for every distance of the A_3) the proper energy of the associating atoms. We shall use in what follows the following coordinates: the components the vector $\mathbf{q}_{12}$ pointing from A_1 to A_2, the components of $\mathbf{q}_3$ connecting A_3 with the center of mass of A_1 and A_2, and finally the components of the vector $\mathbf{Q}$ pointing to the center of mass of all three atoms. The corresponding momenta are $\mathbf{p}_{12}$, $\mathbf{p}_3$, $\mathbf{P}$;

$$H_0=\frac{1}{2m_r}\mathbf{p}_{12}^2+V_0, \tag{6}$$

where m_r is the relative mass of the associating atoms $1/m_r=1/m_1+1/m_2$ and $V_0(r_{12})$ is the potential energy $V(r_{12}, r_{13}, r_{23})$ for $r_{13}=r_{23}=\infty$. Thus

$$H-H_0=\frac{1}{2\mu}\mathbf{p}_3^2+\frac{1}{2M}\mathbf{P}^2+V-V_0, \tag{7}$$

where $1/\mu=1/(m_1+m_2)+1/m_3$ and M is the mass of all three atoms together.

We have then by (2)

$$\frac{dH_0}{dt}=-\frac{1}{m_r}(\mathbf{p}_{12}, \operatorname{grad}_{12}(V-V_0)) \tag{8}$$

and,

$$I(E)=\int\cdots\int_{H_0<E}(1/m_r)(\mathbf{p}_{12}, \operatorname{grad}_{12}(V-V_0)) \cdot e^{-H/kT}d\mathbf{q}_{12}d\mathbf{q}_3d\mathbf{Q}d\mathbf{p}_{12}d\mathbf{p}_3d\mathbf{P}. \tag{9}$$

The integration over $\mathbf{Q}$ gives the total volume v that over $\mathbf{p}_3$ and $\mathbf{P}$ gives $(2\pi\mu kT)^{\frac{1}{2}}(2\pi MkT)^{\frac{1}{2}}$. One can perform an orthogonal transformation for $\mathbf{p}_{12}$ making p_{12x} parallel to $\operatorname{grad}_{12}(V-V_0)$. The condition $dH_0/dt<0$ means that the scalar product in (9) is positive, i.e., that p_{12x} has the sign of the grad. The conditions $H_0<E$ means $p_{12x}^2+p_{12y}^2+p_{12z}^2<2m_r(E-V_0)$. Thus (9) becomes

$$I(E)=(2\pi kT)^3v(\mu M)^{\frac{1}{2}}m_r^{-1}\int d\mathbf{q}_{12}\int_{H_0<E,\ p_{12x}>0}d\mathbf{q}_3\int d\mathbf{p}_{12} \cdot p_{12x}|\operatorname{grad}_{12}(V-V_0)| \cdot\exp(-\mathbf{p}_{12}^2/2m_rkT-V/kT).$$

The integration over p_{12x} can be performed immediately and that over p_{12y} and p_{12z} also if one introduces polar coordinates in the $p_{12y}p_{12z}$ plane. One obtains

$$I(E)=(2\pi kT)^4kTvm_r(\mu M)^{\frac{1}{2}} \cdot\int_{V_0<E}d\mathbf{q}_{12}\int d\mathbf{q}_3|\operatorname{grad}_{12}(V-V_0)| \cdot\{\exp(-V/kT)-[1+(E-V_0)/kT] \cdot\exp[-(E+V-V_0)/kT]\}. \tag{10}$$

For (5), we have to differentiate this with respect to E. Differentiating with respect to the limit of integration involves setting $V_0=E$ in the integrand, which vanishes hereupon. Differentiating inside with respect to E, setting $E=0$ and dividing by $Z/v^2=v(2\pi kT)^{\frac{3}{2}}(m_1m_2m_3)^{\frac{1}{2}}$ gives $(m_1m_2m_3=m_r\mu M)$

$$k=(2\pi m_rkT)^{-\frac{1}{2}}\int_{V_0<0}d\mathbf{q}_{12}\int d\mathbf{q}_3 \cdot|\operatorname{grad}_{12}(V-V_0)|(-V_0/kT)e^{-(V-V_0)/kT}. \tag{11}$$

If the associating atoms are different and there are n_1 and n_2 of them in the volume v, and n_3 of the third body, the number of effective collisions will be $n_1n_2n_3$ times (11), i.e., the rate constant is given by (11). If the associating atoms are identical and their number n, the number of effective collisions will be $(n(n-1)/2)n_3$ times (11). Thus in case of the formation of a symmetrical molecule the well-known factor $\frac{1}{2}$ must be applied to (11). In addition to this, in most cases the reaction can occur only for definite relative orientations of the angular momenta of the atoms and this must be taken care of by another factor giving the probability of such an orientation. It may be pointed out again that (11) is only an upper limit for the rate of association and one could probably somewhat lower it by choosing H_0 more appropriately.

5

Equation (11) gives always an upper limit for the rate of association. However, if $V-V_0$ can assume negative values, this upper limit can be lowered somewhat quite easily. Indeed, in a system formed by three atoms, the total relative energy $H_r=H-\mathbf{P}^2/2M$ never can be negative

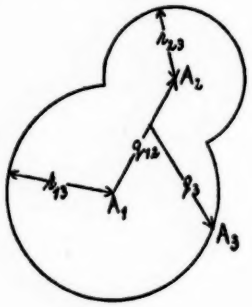

FIG. 1.

and it is not necessary, therefore, to include systems with negative energy into the assembly.

For large distance of the third body, naturally $H_r>H_0$. However, at $\mathbf{p}_3^2/2\mu+V-V_0=0$ the $H_r=0$ surface cuts the $H_0=0$ surface and goes above it. It is a better choice for S, then, to use the $H_r=0$ surface where it lies above the $H_0=0$ surface, than this one, because no system can go through the $H_r=0$ surface, H_r being (apart from the influence of the walls) an integral of the motion.

The integration of (9) over $\mathbf{p}_3$ should not be extended, therefore, over the region $\mathbf{p}_3^2/2\mu+V-V_0<0$ in (9) and a factor

$$\int_{p_3^2>2\mu(V_0-V)} \exp(-\mathbf{p}_3^2/2\mu kT)d\mathbf{p}_3 \Big/ \int_0^\infty \exp(-\mathbf{p}_3^2/2\mu kT)d\mathbf{p}_3 = 1-F((V_0-V)^{\frac{1}{2}}/(kT)^{\frac{1}{2}}) +2((V_0-V)/\pi kT)^{\frac{1}{2}}e^{-(V_0-V)/kT} \quad (12)$$

can be inserted to the integrand of (11) wherever V_0-V is positive. F is the error integral

$$F(x)=\frac{2}{\pi^{\frac{1}{2}}}\int_0^x e^{-x^2}dx. \quad (13)$$

Another improvement can be made on (11) if the attractive region of V_0 is preceded by a repulsive part. However, since it is a rather rare occurrence, it will not be discussed further.

6

If the third body is an inert gas, the total potential energy is the sum of the interactions of the three pairs of atoms. $V-V_0=V_{13}(r_{13})+V_{23}(r_{23})$ is positive in these cases and the correction (12) cannot be applied. The integrand of (11), as function of q_3 has a rather sharp maximum on two spherical portions, represented in Fig. 1. The radius r_{13} of the sphere around A_1 is the sum a_{13} of the collision radii of A_1 and A_3, similarly r_{23} is the sum a_{23} of the collision radii of A_2 and A_3. On the first sphere, one can introduce instead of q_3 polar coordinates around A_1. Integration over the polar angles gives the solid angle α_{13} of the first spherical portion. This is

$$\alpha_{13}(q_{12})=\pi[(a_{13}+q_{12})^2-a_{23}^2]/a_{13}q_{12} \quad (14a)$$

for $q_{12}<a_{13}+a_{23}$ and

$$\alpha_{13}(q_{12})=4\pi \quad (14b)$$

for $q_{12}>a_{13}+a_{23}$. On the sphere around A_1, one can set $V-V_0=V_{13}(r_{13})$, and the derivative of this, with respect to q_{12}, at constant q_3, is $m_2/(m_1+m_2)$ times the derivative with respect to r_{13}. Taking the factor $a_{13}^2\alpha_{13}(q_{12})$ out of the integral, one must integrate $|\partial V_{13}/\partial r_{13}|\exp(-V_{13}/kT)$ with respect to r_{13} between 0 and ∞, which gives just kT. One obtains, performing a similar transformation on the sphere around A_2 also,

$$k=-\frac{(2\pi m_r kT)^{-\frac{1}{2}}}{m_1+m_2}\int_{V_0<0} dq_{12} \cdot V_0[m_2a_{13}^2\alpha_{13}(q_{12})+m_1a_{23}^2\alpha_{23}(q_{12})] =-2\pi\left(\frac{2\pi m_r}{kT}\right)^{\frac{1}{2}}\int_{V_0<0} V_0q_{12}\{(a_{13}^2-a_{23}^2) \cdot(a_{13}/m_1-a_{23}/m_2)+2(a_{13}^2/m_1+a_{23}^2/m_2)q_{12} +(a_{13}/m_1+a_{23}/m_2)q_{12}^2\}dq_{12}. \quad (15)$$

In the last expression, (14a) has been used throughout because in most practical cases V_0 is very small for $q_{12}>a_{13}+a_{23}$.

This equation will be compared with the experimental results of Rabinowitch and W. C.

Wood[9] on the recombination of iodine atoms.

For V_0 the Morse curve was used

$$V_0 = D(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}) \qquad (16)$$

with[10] $D = 2.46 \cdot 10^{-12}$ erg, $\alpha = 1.83 \cdot 10^8$ cm^{-1}, $r_0 = 2.66 \cdot 10^{-8}$ cm. This gives

$$-\int V_0 q_{12}^2 dq_{12} = 2.7 \cdot 10^{-35} \text{ erg cm}^3$$

and

$$-\int V_0 q_{12}^3 dq_{12} = 0.91 \cdot 10^{-42} \text{ erg cm}^4.$$

In this case, $a_{13} = a_{23} = r_J + r_3$ and the values shown in Table I were adopted for the radii.[11] The last line gives the values calculated by (14). These must be divided first by 2, because the associating molecules are identical, and next by 16, because only one of the ten states formed by two $^2P_{3/2}$ iodine atoms leads to the normal state of the molecule. The experimental results are compared with the calculated ones in Table II.

Although the disagreement is not very great, it is important to notice that the calculated values are lower throughout than the experimental ones. For the molecules H_2, N_2, O_2 this is, perhaps, not so serious, because (15) should hold for atoms only.[12] For He and A, however, (15) should definitively give an upper limit for the reaction rate. The calculated values should be indeed materially higher than the observed ones.

One possible source of error is contained in the radii of Table I. It would seem, however, that these hardly can be in error by a sufficient amount to explain the discrepancy. The second source of error lies in the potential curve (16). It cannot be expected, of course, that the Morse curve be accurate throughout. In fact, if one determines the α of (16) from the anharmonicity of the vibration instead of dissociation energy and vibrational frequency,[13] one obtains $1.47 \cdot 10^8$ cm^{-1}. This would compensate the discrepancy. However, the curve of Brown[14] for V_0 integrated directly, gives practically the same result as (16).

It is possible also that not only a O_g^+ state is strongly attractive among the 10 different states arising from two $^2P_{3/2}$ iodine atoms. Although all states known so far are either repulsive or only very weakly attractive, this possibility must be left open. No such difficulty would come up at the calculation of the rate of recombination of H atoms, e.g., since all states are known in that case.

TABLE I.

	He	A	H_2	N_2	O_2
$r \cdot 10^8$	1	1.43	1.09	1.58	1.48
$k \cdot 10^{31}$	4.5	6.5	5.4	7	6.7

TABLE II.

	He	A	H_2	N_2	O_2
calc. $k \cdot 10^{31}$	0.14	0.20	0.17	0.22	0.21
exp " "	0.18	0.36	0.40	0.66	1.05

There is one more point which should be mentioned. For very large q_{12}, the Morse curve is not valid and the attraction due to the magnetic moment of the spins decreases only as the inverse third power of q_{12}. Since the square bracket of (15) becomes $8\pi m_2 a_{13}^2$ for very large q_{12}, the integral appears to diverge logarithmically. It does not appear sensible, however, to consider two atoms as forming a molecule if, in all probability, they will suffer a dissociating collision before completing a vibration. One is thus led to extending the integration over q_{12} to the mean free path only. The contribution of the magnetic dipole forces then becomes negligible and the breaking down of (15) (caused by the incorrect situation of S) does not become serious.

[9] E. Rabinowitch and W. C. Wood. J. Chem. Phys. **4**, 497 (1936).

[10] Cf. for the spectroscopic data, H. Sponer, *Molekülspektren* (Berlin, 1936), Vol. I, p. 18.

[11] Cf. Landolt-Börnstein's Tables, 1st Ergänzungsband, p. 69. The radius of Xe, i.e., 1.75A, was used for J.

[12] In addition to this, the formation of an intermediate iodide of the third body may be considered. Cf. reference 9.

[13] For a discussion of this and related questions, cf. reference 10, Vol. 2, p. 103 f.

[14] W. G. Brown, Phys. Rev. **38**, 1187 (1931).

[15] Cf. reference 14, also J. H. Van Vleck, Phys. Rev. **40**, 544 (1932).

Theory of the Viscosity of Liquids as a Function of Temperature and Pressure

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An equation for the viscosity of a liquid in terms of the energy of vaporization and the molal volume is developed from the reaction rate theory of viscosity due to Eyring. The degree of freedom corresponding to flow is assumed to be a translational one, and the energy of activation for the elementary flow process is assumed to be some fraction, $1/n$, of the energy of vaporization. On applying this equation to a large number of normal liquids it is found that molecules possessing spherical symmetry have $n=3$, while nonspherical molecules have n greater than 3, usually about 4. It is shown that the ratio

$$\Delta E_{\text{vap}}/\Delta E_{\text{vis}}, \quad \text{where} \quad \Delta E_{\text{vis}}=R(d\ln\eta)/(d(1/T)),$$

can be taken as an index of the size and shape of the molecule, or more precisely, of the unit of flow in the liquid. The activation energy for flow in liquid metals is a very small fraction of the energy of vaporization, ranging from 1/10 to 1/25, leading to the conclusion that the metal ions flow without their valence electrons. Viscosity data confirm the S_8 ring structure for sulfur below 160° and lead to the conclusion that above 250° sulfur probably consists of long chains containing as a rough average about 36 sulfur atoms. In the long chain hydrocarbons the activated configuration for flow is probably a curled up molecule. The structure activation energy of flow in associated liquids due to the hydrogen bond structure is discussed, and viscosity data are used to compute the degree of coordination in liquid water. At high pressures the energy of vaporization in the equation must be replaced by $V(p_{\text{internal}}+p_{\text{external}})$. This yields an equation for computing either the internal pressure of a liquid or the viscosity under pressure, if either is known. Using Bridgman's viscosity data, values of the internal pressures of some liquids are calculated from this equation which agree with internal pressures calculated from compressibility data.

BY considering viscous flow as a chemical reaction in which the elementary process is the passing of a single molecule from one equilibrium position to another over a potential barrier, Eyring[1] has developed the general equation:

$$\eta=\frac{\lambda_1 h}{\kappa\lambda^2\lambda_2\lambda_3}\frac{F_n}{F_a^*}\exp\frac{\Delta E_{\text{act}}}{kT}, \tag{1}$$

where

λ = distance between equilibrium positions in the direction of flow,
λ_1 = perpendicular distance between adjacent layers of molecules,
λ_2 = distance between adjacent molecules in the direction of flow,
λ_3 = distance between molecules in the plane of flow and normal to the direction of flow,
κ = transmission coefficient,
F_n = partition function of normal molecule,
F_a^* = partition function of the activated molecule, omitting the degree of freedom corresponding to flow,
ΔE_{act} = activation energy for the flow process.

κ is usually unity for chemical reactions and will be so assumed in this development. If λ, the distance between equilibrium positions, is equal to λ_1 we have

$$\lambda_1/\lambda^2\lambda_2\lambda_3=N/V,$$

where N is Avogadro's number and V is the molar volume.

If we assume that the degree of freedom corresponding to flow is a translational one and other degrees of freedom are the same for the initial and activated states:

$$\frac{F_n}{F_a^*}=\frac{\dfrac{(2\pi mkT)^{\frac{1}{2}}}{h^3}V_f F_{\text{rot}}F_{\text{vib}}}{\dfrac{2\pi mkT}{h^2}V_f^{\frac{1}{3}}F_{\text{rot}}F_{\text{vib}}}=\frac{(2\pi mkT)^{\frac{1}{2}}}{h}V_f^{\frac{1}{3}} \tag{2}$$

where V_f = the free volume. Eyring and Hirschfelder[2] have formulated the free volume

$$V_f^{\frac{1}{3}}=\frac{bRT}{V^{\frac{1}{3}}N^{\frac{1}{3}}(p+a/V^2)}\ \text{per molecule}$$

$$=\frac{bRTV^{\frac{1}{3}}}{N^{\frac{1}{3}}\Delta E_{\text{vap}}} \quad \text{if} \quad \frac{a}{V^2}=\frac{\Delta E_{\text{vap}}}{V}\gg p, \tag{3}$$

where

[1] Eyring, J. Chem. Phys. **4**, 283 (1936).

[2] Eyring and Hirschfelder, J. Phys. Chem. **41**, 249 (1937).

ΔE_{vap} = energy of vaporization = $\Delta H_{vap} - \Delta(pV)$.
$b = 2$ for simple cubic packing and has not very different values for other types of packing.

For a molecule to flow it must have a hole to flow into, but this may not necessarily have to be a hole the full size of a molecule. Therefore the activation energy for viscous flow will be some fraction of the energy of vaporization, $\Delta E_{act} = \Delta E_{vap}/n$, since ΔE_{vap} is the energy required to make a hole in a liquid the size of a molecule. Combining all these evaluations of the quantities in Eq. (1) we get

$$\eta = \frac{Nh}{V}\frac{(2\pi mkT)^{\frac{1}{2}}}{h}\frac{bRTV^{\frac{1}{3}}}{N^{\frac{1}{3}}\Delta E_{vap}}\exp\frac{\Delta E_{vap}}{nRT}$$

$$= 1.090\cdot 10^{-3}\frac{M^{\frac{1}{2}}T^{\frac{1}{2}}}{V^{\frac{1}{3}}\Delta E_{vap}}\exp\frac{\Delta E_{vap}}{nRT} \qquad (4)$$

if we take $b = 2$, and R and ΔE_{vap} are in calories per mole.

In order to test Eq. (4) and for use elsewhere in this paper careful selections of density and heat of vaporization data were made from the values given in the Landolt-Börnstein *Tabellen*. In many cases it was necessary to plot the various values of the heats of vaporization against the temperature and draw a best straight line or curve through the points for interpolation purposes. E_{vap} was obtained from ΔH_{vap} by subtracting $\Delta(pV)$ of vaporization. The viscosity data used to test Eq. (4) and elsewhere in this paper were from the following sources:

Most organic liquids, Thorpe and Rodger, Trans. Roy. Soc. (London) **185A**, 307 (1894) and **189A**, 71 (1897), Timmermanns and co-workers, J. chim. phys. (1926–35).
A, CH_4, N_2, CO, O_2, C_2H_4, Rudenko and Schubnikov, Physik. Zeits. Sowjetunion **6**, 470 (1934) and **8**, 179 (1935).
C_9H_{20}, $C_{10}H_{22}$, $C_{11}H_{24}$, Bingham and Fornwalt, J. Rheol. **1**, 372 (1930).
$C_{14}H_{30}$, $C_{16}H_{34}$, $C_{18}H_{38}$, Ubbelohde and Agthe, quoted in Engler-Höfer, *Das Erdöl* Vol. 1 (Berlin 1913), p. 53.
Sulfur, Rotinjanz, Zeits. f. physik. Chemie **62**, 609 (1908).
Na, K, Chiong, Proc. Roy. Soc. (London) **157A**, 264 (1936).
Hg, Erk, Zeits. f. physik. Chemie **47**, 886 (1928).
Ga, Spells, Proc. Phys. Soc. (London) **48**, 299 (1936).
Ag, Zn, Cd, Gering and Sauerwald, Zeits. f. anorg. allgem. Chemie **223**, 204 (1935).
Sn, Stott, Proc. Phys. Soc. (London) **45**, 530 (1933).
Pb, Esser, Greis and Bungardt, Arch. Eisenhuttenuw **7**, 385 (1934).
H_2O, *International Critical Tables* V, 10.

The Temperature Variation of Viscosity and the Value of n

Using the data mentioned in the last section Eq. (4) was used to compute the viscosity of a number of liquids over a range of temperatures using half-integral values of n from 2 to 5. In order to ascertain which value of n gave the correct temperature coefficient, the computed values of the viscosity were plotted as $\log \eta$ against $1/T$. It is a well-known empirical fact that for all normal liquids $\eta = Ae^{B/T}$ where A and B are constant so that $\log \eta$ plotted against $1/T$ is a straight line. For any value of n the computed viscosities gave a $\log \eta$ *vs.* $1/T$ plot which was a straight line or in some cases very slightly convex towards the $1/T$ axis. The value of n which gave a plot parallel to the straight line of the observed viscosities was taken as the value of n which gave the correct temperature coefficient. These calculations were carried out for all the liquids for which fairly reliable heats of vaporization over a range of temperatures were known. The results to the closest half-integer are given in Table I. In most cases the $\log \eta$ *vs.* $1/T$ plot for the value of n given in Table I was nearly exactly parallel to the observed, and in a few cases where the plots were slightly divergent there was no doubt as to which was the closest half-integral value for n. As examples, Table II shows the calculations for CCl_4 and Fig. 1 shows the plots for CCl_4, N_2, C_6H_{14}, $CHCl_3$. Computations similar to Table II and plots similar to Fig. 1 were made for all the liquids listed in Table I.

Table I.

$n = 3$	CCl_4, C_6H_6, cyclohexane, CH_4, N_2, CO, A
$n = 3\frac{1}{2}$	$C_2H_4Cl_2$, $C_2H_4Br_2$, O_2*
$n = 4$	pentane, hexane, heptane, CS_2, $CHCl_3$, $C_6H_5CH_3$, ether, ethyl acetate, acetone, C_2H_5I, C_2H_5Br, CH_3I, C_2H_4

* The anomaly of O_2 as compared to N_2 and CO may be attributed to its paramagnetic property. No explanation is offered for the result for the ethylene halides.

The fact that there is a sharp separation into two classes of liquids (except O_2, $C_2H_4Cl_2$, $C_2H_4Br_2$) with $n = 3$ and $n = 4$, respectively, is significant. Most of the $n = 3$ liquids have spherical or approximately spherical fields of force. This is certainly true of CCl_4, CH_4 and A, and is very nearly true of N_2 and CO when the

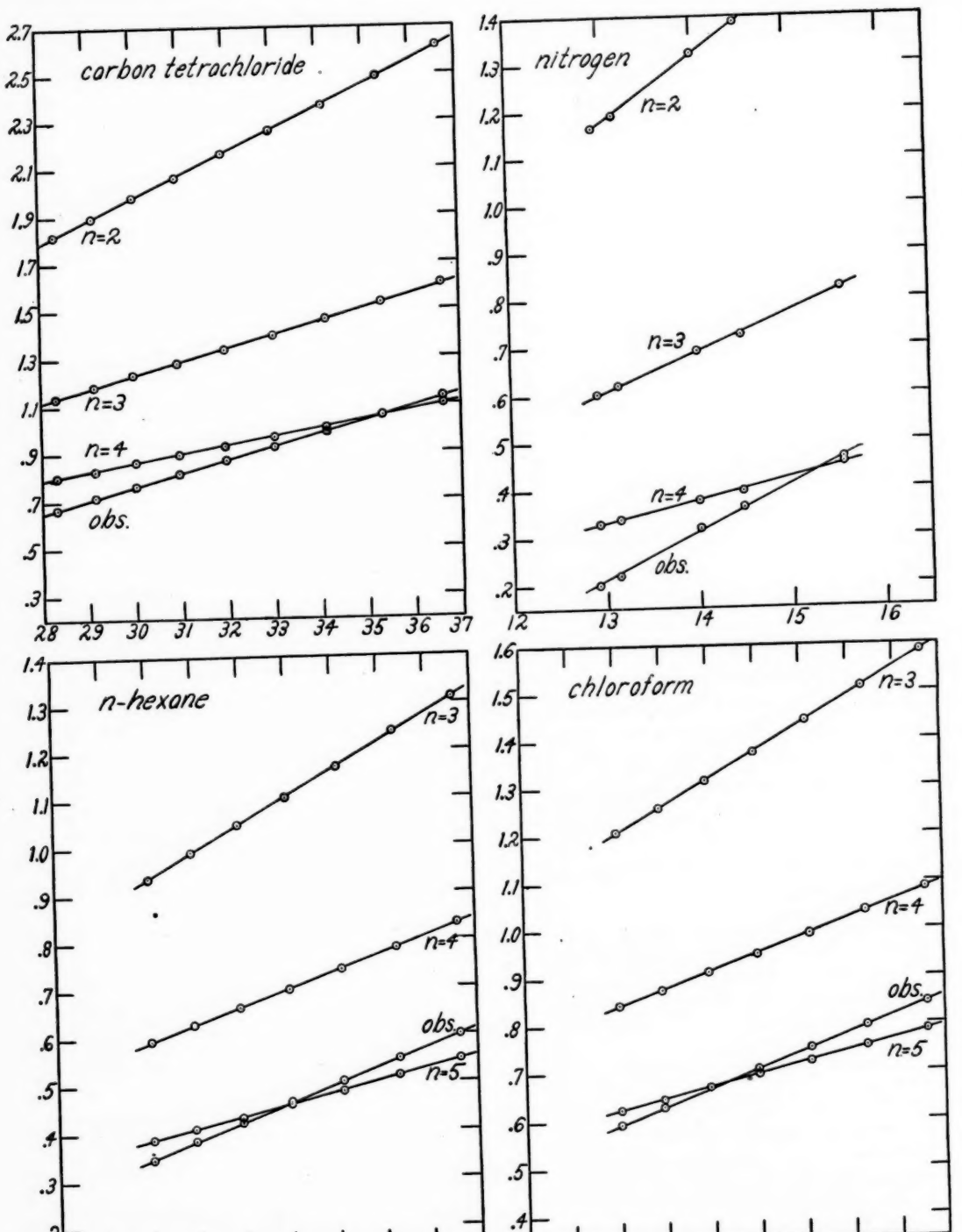


FIG. 1. Plots of log η *vs.* $1/T$ for observed and calculated viscosities, using integral values of n in Eq. (4).

probable shape of the potential energy surface at kinetic energy levels is considered. There is also considerable evidence that benzene is not the conventional flat hexagon, but that it has approximately a spherical field of force.[3] Bernal[4] has classified cyclohexane as a spherical molecule for reasons which he does not state, and the present result might be considered as confirming the spherical character of cyclohexane. The fact that the activation energy for flow is just one-third the energy of vaporization for these spherical molecules leads to the interesting and useful concept that viscous flow is a sort of vaporization in one degree of freedom.

The other group of liquids with $n=4$, however, are not of spherical symmetry and most of them are polar. For spherical molecules, where all orientations are equivalent, the activation energy of flow is the energy required to make a hole one-third the size of a molecule, i.e., $\Delta E_{vap}/3$, while for polar or elongated molecules where certain preferred orientations are possible a smaller fraction of the energy of vaporization is sufficient for activation. Naturally if there is a possibility of several orientations the molecule will assume that orientation during flow which requires the least activation energy. That this activation energy should be very close to one-fourth the energy of vaporization for such a wide variety of molecules is an interesting fact.

It will be noted that while the plots with $n=3$ and $n=4$ in Fig. 1 are found to be parallel to the observed, indicating the correct temperature coefficient, the parallel plots do not coincide. Viscosities calculated using Eq. (4) are always higher than the observed and the antilogarithms of the difference in ordinate of the parallel plots is the factor by which the calculated values are too large. For most liquids the calculated values are too large by a factor of 2 or 3, when the value of n giving the correct temperature coefficient is used. When higher or lower values of n are used, the calculated values are much lower or higher, respectively, as shown in Fig. 1.

This factor of 2 or 3 may be due to several errors in the assumptions we have made. The transmission coefficient, κ, may not be unity, but deviations from unity would make the error even greater. The packing factor, b, may not be 2, but it would not be very different for types of packing other than simple cubic. A quite possible explanation is that a flowing molecule may possess a "persistence of velocity" and when it has once acquired the necessary activation energy it may move more than one intermolecular distance, and λ may be equal to λ_1, $2\lambda_1$, $3\lambda_1$, etc. for any individual elementary process. It would only be necessary for λ to equal $2\lambda_1$ in 40 percent of the elementary processes to give a calculated viscosity too large by a factor of 2, or in 70 percent of the processes for a factor of 3.

Another possible explanation is that the flow process may be a bimolecular process rather than a unimolecular one, at least in part. According to this mechanism two molecules in adjacent layers, which are moving relative to one another, temporarily form a pair which rotates through an angle of about 90°. The relative motion of successive layers in the liquid is the resultant of many such rotations of pairs of molecules. During the rotation the two molecules will sweep out a volume ΔV, which is the extra volume

[3] See Mack, J. Phys. Chem. **41**, 221 (1937).
[4] Bernal, Trans. Faraday Soc. **33**, 27 (1937).

TABLE II. *Computation of viscosity of CCl_4*

					$n=2$		$n=3$		$n=4$	
t°C	T°K	V cc/mole	ΔEvap kcal./mole	η(obs.) millipoises	η(calc.) millipoises	η(calc.)/η(obs.)	η(calc.) millipoises	η(calc.)/η(obs.)	η(calc.) millipoises	η(calc.)/η(obs.)
0	273.1	94.3	7.56	13.47	413	30.7	40.3	2.99	12.7	0.95
10	283.1	95.4	7.43	11.33	305	26.9	33.8	2.98	11.3	1.01
20	293.1	96.6	7.30	9.69	232	24.0	28.8	2.98	10.1	1.04
30	303.1	97.8	7.18	8.42	182	21.6	24.8	2.95	9.2	1.08
40	313.1	99.0	7.06	7.38	145	19.7	21.7	2.94	8.5	1.13
50	323.1	100.3	6.93	6.53	115	17.6	19.1	2.92	7.8	1.19
60	333.1	101.6	6.81	5.84	96	16.4	17.1	2.93	7.3	1.24
70	343.1	103.0	6.68	5.24	78	14.9	15.3	2.92	6.7	1.28
80	353.1	104.4	6.56	4.68	66	14.2	13.8	2.95	6.4	1.36

necessary for the elementary process to take place and would obviously be $V/3$ and $V/4$ of the two classes of molecules. For this bimolecular mechanism, Eq. (1), would be written

$$\eta=\frac{\lambda_1 h}{\kappa\lambda^2\lambda_2\lambda_3}\frac{F_n^2}{F_a'^*}\exp\frac{\Delta E_{act}}{kT},$$

where $F_a'^*$ is the partition function of the bimolecular activated complex, omitting the degree of freedom corresponding to flow. If

$$\frac{F_n^2}{F_a'^*}=\frac{F_n}{F_a^*}=\frac{(2\pi mkT)^{\frac{1}{2}}}{h}V_f^{\frac{1}{3}}$$

the two mechanisms are equivalent, but if

$$\frac{F_n^2}{F_a'^*}<\frac{(2\pi mkT)^{\frac{1}{2}}}{h}V_f^{\frac{1}{3}}$$

the viscosities calculated on the basis of the unimolecular mechanism would be too large.

All these factors might be collected into one parameter in the denominator of Eq. (1)

$$a=b\lambda^2/2\kappa\lambda_1^2$$

if the unimolecular mechanism is retained, or

$$a=(b\lambda^2/2\kappa\lambda_1^2)(F_a'^*/F_nF_a^*)$$

if the bimolecular mechanism is assumed, giving Eq. (1) with two parameters a and n. The following are the approximate factors by which the calculated viscosities are too high, i.e., values of the parameter a: CCl_4 3.00, C_6H_6 3.50, cyclohexane 2.05, CH_4 3.50, A 2.30, N_2, 2.40, CO 2.50, pentane 1.73, hexane 1.75, heptane 2.00, CS_2 1.91, ether 2.00, ethyl acetate 2.05, toluene 2.05, acetone 2.20.

Further elucidation of the discrepancy between the observed viscosities and those given by the theory will not be undertaken at this time. The fact that the factors just given are about the same for all liquids and the success of the theory in interpreting the temperature coefficient of viscosity show that the reaction rate theory is essentially correct and that if the elementary process is a bimolecular one it is essentially equivalent to the unimolecular mechanism assumed in the treatment in this paper.

TABLE III.

LIQUID	ΔE_{vis} CAL./MOLE	ΔE_{vap} AT B.P. CAL./MOLE	$\frac{\Delta E_{vap}}{\Delta E_{vis}}$	n
CCl_4	2500	6600	2.66	3
C_6H_6	2540	6660	2.62	3
Cyclohexane	2890	6700	2.32	3
CH_4	719	1820	2.53	3
A	516	1420	2.75	3
N_2	449	1210	2.70	3
CO	466	1310	2.80	3
O_2	398	1470	3.69	$3\frac{1}{2}$
$C_2H_4Cl_2$	2270	6930	3.05	$3\frac{1}{2}$
$C_2H_4Br_2$	2590	7890	3.04	$3\frac{1}{2}$
Pentane	1580	5510	3.50	4
Hexane	1715	6220	3.61	4
$CHCl_3$	1760	6630	3.76	4
C_2H_5I	1720	6400	3.72	4
C_2H_5Br	1585	6080	3.84	4
CS_2	1280	5920	4.63	4
$C_6H_5CH_3$	2120	7240	3.42	4
Ether	1610	5700	3.54	4
Acetone	1655	6400	3.86	4
C_2H_4	793	3500	4.41	4

Comparison of n with the ratio $\Delta E_{vap}/\Delta E_{vis}$

In the empirical equation $\eta=Ae^{B/T}$, A is an entropy factor and B is an energy factor. In the flow process as in rate processes generally, energy and entropy of activation tend to compensate each other in such a way as to give the smallest possible free energy of activation. The last section showed that A and B are not constants, but are functions of the temperature (and pressure, too, as will be discussed later), and the nature of the functions was deduced. The fact that A and B appear empirically to be constants over a considerable temperature range is not a coincidence, but is the result of the compensating effect of the energy and entropy of activation making the free energy of activation practically independent of temperature.

If we write $\eta=Ae^{\Delta E_{vis}/RT}$, ΔE_{vis} will be the experimentally determined quantity $Rd\ln\eta/d(1/T)$. Since this is a constant for normal liquids throughout their normal liquid range, ΔE_{vis} can be considered as an average activation energy of flow in this range. Since ΔE_{vap} varies only slowly with temperature, the ratio $\Delta E_{vap}/\Delta E_{vis}$ should be approximately equal to 3 or 4 anywhere in the temperature range where ΔE_{vis} is a constant. Table III gives a comparison of n (as determined in the preceding section) with $\Delta E_{vap}/\Delta E_{vis}$, where ΔE_{vap} is taken at the normal boiling point for all the liquids in the table.

It is seen that for all the $n=3$ liquids $\Delta E_{vap}/\Delta E_{vis}$ ranges from 2.3 to 2.8, and for all the $n=4$ liquids from 3.4 to 3.9 (except CS_2 and C_2H_4 which are still higher). If the comparison had been made at a lower corresponding temperature, e.g., about four-fifths the absolute boiling

TABLE IV.

METAL	MIDDLE OF TEMP. RANGE OF VISCOSITY DATA	ΔE_{vap} KCAL./MOLE	ΔE_{vis} KCAL./MOLE	$\frac{E_{vap}}{E_{vis}}$	$\frac{\Delta E_{vap}}{\Delta E_{vis}}\left(\frac{r_{ion}}{r_{atom}}\right)^3$
Na	500°	23.4	1.45	16.1	2.52
K	480°	19.0	1.13	16.7	3.41
Ag	1400°	60.7	4.82	12.5	3.79
Zn	850°	26.5	3.09	8.6	2.10
Cd	750°	22.5	1.65	13.5	3.96
Hg	250°	13.6	0.65	20.8	2.37
	600°	12.3	0.55	22.2	2.54
Ga	800°	34.1	1.13	30.3	2.53
Sn	600°	15.3	1.44	10.6	4.07
	1000°	14.5	1.70	8.6	3.30
Pb	700°	42.6	2.80	15.9	4.97

point, all the values of the ratio would have been higher (since ΔE_{vap} would be larger), and the values of the ratio would have clustered around 3 for the $n=3$ liquids and around 4 for the $n=4$ liquids (except C_2H_4 and CS_2). These results show that the value of the experimentally determined ratio $\Delta E_{vap}/\Delta E_{vis}$ at any temperature may be taken as a rough index of the size and shape of the molecule, or more precisely, of the unit of flow. If the value of $\Delta E_{vap}/\Delta E_{vis}$ is much larger than 3 or 4, it indicates that the unit of flow is much smaller than the unit of vaporization (which can be taken as the single molecule in most cases), and if $\Delta E_{vap}/\Delta E_{vis}$ is much smaller than 3 or 4, the reverse is indicated. Examples of both these cases will be discussed below.

Liquid metals

Most metals give linear $\log \eta$ *vs.* $1/T$ plots, just as normal covalent liquids do. A few metals, however, notably mercury and tin exhibit a slight curvature. The most striking fact regarding the metals is the large value of the $\Delta E_{vap}/\Delta E_{vis}$ ratio, which ranges from 8 to 25 for different metals as compared to the value of 3 or 4 for normal liquids. This means that the activation energy for flow is much less than $\Delta E_{vap}/3$ and leads to the conclusion that the unit of flow is much smaller than the unit of vaporization. The unit of vaporization is the atom, of course, and the unit of flow must then be the much smaller metal ion, i.e., the atom stripped of its valence electron or electrons.

On this hypothesis the activation energy of flow, ΔE_{vis}, would be

$$\frac{\Delta E_{vap}}{3}\times\frac{\text{volume of ion}}{\text{volume of atom}}=\frac{\Delta E_{vap}}{3}\left(\frac{r_{ion}}{r_{atom}}\right)^3$$

or $\Delta E_{vap}/\Delta E_{vis}(r_{ion}/r_{atom})^3$ should be equal to 3, assuming the metal ions would have spherical symmetry. Table IV shows the experimental values of this latter quantity, using the ionic and atomic radii given by Wyckoff.[5] The heats of vaporization of metals are not very reliable and are usually not known over a range of temperature. When the temperature variation was known, ΔE_{vap} was taken arbitrarily in the middle of the range over which the viscosities were measured (shown in column 2). In the case of Hg and Sn the average slopes over the two halves of the slightly curved $\log \eta$ *vs.* $1/T$ plot are given. For the polyvalent metals the following ions were assumed to be the flowing ion: Hg^+, Sn^{++}, Pb^{++}.

While the figures in column 6 are not all equal to 3, they do cluster around 3 and are much closer to 3 than are the figures in column 5, and further, the deviations from 3 are not much greater than the uncertainties in the experimental quantities used in the table. While this

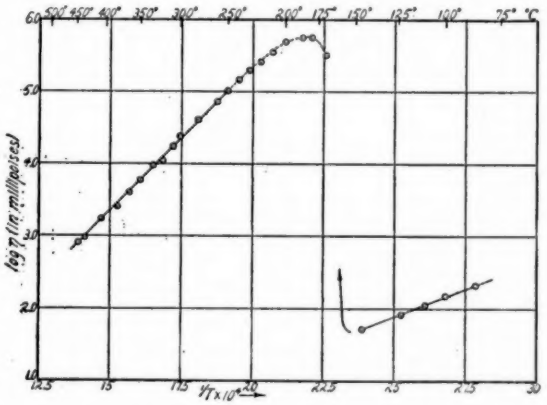


FIG. 2. Plot of $\log$ *vs.* $1/T$ for liquid sulfur from the data of Rotinjanz.

[5] Wyckoff, *The Structure of Crystals* (Reinhold Publishing Co., 1931).

result is interesting and suggestive, the hypothesis must not be taken too literally. Since the energy of vaporization of a metal atom is made up of separate work functions of the ion and the electron or electrons, it cannot be so definitely interpreted as the energy necessary to make a hole the size of an atom in the liquid, as in the case of normal covalent liquids. The qualitative concept of the metal ions flowing free of their valence electrons is, of course, quite in harmony with modern ideas on the structure of metals.

Liquid sulfur

As is well known liquid sulfur is a fluid yellow liquid between the melting point and about 160° and also in the supercooled liquid region below the melting point. Above 160° the viscosity increases rapidly, increasing several thousandfold between 160 and 190°, and thereafter the viscosity decreases in a normal way. The numerous theories advanced to explain these phenomena will not be discussed here. Fig. 2 shows the data of Rotinjanz[6] plotted log η against $1/T$. Rotinjanz's data show that between 160 and 250° the viscosity of sulfur is a function of the time as well as the temperature, and the values given in that range are only rough averages and probably not equilibrium values.

It is seen that the plot has two linear portions, below 160 and above 250°, for which ΔE_{vis} is 7.04 and 18.35 kcal./mole, respectively. In the region below 160° the molecule is almost certainly a puckered S_8[7] ring, and by comparing this structure with cyclohexane, it seems likely that n would be 3 for this type of molecule. The heats of vaporization of sulfur have been accurately measured by West and Menzies.[8] Their value of ΔE_{vap} at 120° (the middle of this linear part of the plot) is 2.59 kcal./g atom or 20.7 kcal./mole of S_8. This is very nearly three times 7.04 the value of ΔE_{vis} in this range, and this may be considered as further evidence toward confirming the S_8 molecule in the liquid in this range.

In the range above 250° the much larger slope of the curve indicates that the molecule is much larger than it is below 160°. This larger sulfur molecule might be either a large ring, a branched chain or a long straight chain, of which the latter seems most likely to be the correct structure. By analogy with the straight chain hydrocarbons, n should be 4 for this type of molecule, and this would indicate a value of ΔE_{vap} of $4\times18.35=73.4$ kcal./mole on our hypothesis. West and Menzies give 2.05 kcal./g atom for ΔE_{vap} at 350° (the middle of this linear part of the curve) and comparing this with the value deduced above the molecular weight of the unit of flow is found to be S_{36}. In contrast to this molecular weight of the unit of flow, the unit of vaporization is still S_8 as shown by vapor density data.

This figure of 36 can be interpreted as an average chain length averaged over all the molecules in the liquid and averaged over the whole temperature range from 250 to 450°. At any temperature there is probably an equilibrium mixture of chains of varying length, and as the temperature is raised the average chain length will become smaller as the equilibrium constant changes. The linear relation between log η and $1/T$ is not a sufficient condition for an unchanging molecular state in a liquid. Normal liquids composed of a single molecular species almost without exception give linear log η *vs.* $1/T$ plots. However, a liquid composed of an equilibrium mixture of several molecular species might also give a linear plot since the equilibrium constant changes according to van't Hoff's equation, which is of the same form of temperature dependence as is the viscosity of a liquid.

The hypothesis had been advanced by Warren and Burwell that the increase in viscosity above 160° is "probably due to the S_8 ring breaking open and forming irregular chains which tangle with one another and give rise to the marked increase in viscosity." Our results give more concrete form to this idea and obviates the necessity of postulating the indefinite concept of tangling of chains since any liquid composed of chains averaging 36 atoms in length, e.g., a hydrocarbon, will be a very viscous liquid.

The normal paraffin hydrocarbons

The values of ΔE_{vis} were determined graphically for the normal paraffins, from pentane to octadecane, using the data mentioned in the list of sources of viscosity data. From pentane to octane the log η *vs.* $1/T$ plots were straight lines

[6] Zeits. f. physik. Chemie **62**, 609 (1908).
[7] Warren and Burwell, J. Chem. Phys. **3**, 6 (1935).
[8] J. Phys. Chem. **33**, 1880 (1929).

as usual, but for nonane and higher the plots were slightly curved (convex towards the $1/T$ axis), the amount of curvature increasing as the length of the chain increased. Therefore the slope was taken over the temperature range of 20 to 40°, except octadecane where the measurements started at 40°. Best values of the heats of vaporization of these hydrocarbons were furnished by Dr. F. D. Rossini of the National Bureau of Standards in a private communication. The uncertainties in these heats varied from ±2 percent for C_5H_{12} to ±6 percent for $C_{18}H_{38}$.

The values of the ratio $\Delta E_{vap}/\Delta E_{vis}$ are given in Table V. The ratio is seen to be about 4 for all these hydrocarbons. This result is surprising and would hardly be possible if these molecules all flowed as extended chain molecules, as a consideration of the mechanism of flow as applied to an extended chain molecule will show. If the hydrocarbon molecules were curled up into a ball shape during the flow process this difficulty would disappear. Such a concept is in harmony with Langmuir's[9] conclusion that molecules are curled up in this way in the vapor state, since flow can be thought of as vaporization in one degree of freedom. This suggests that the liquid hydrocarbon contains both extended and curled up molecules, and the activated molecules which are responsible for flow, diffusion and vaporization of the liquid are of the curled up type.

TABLE V.

HYDROCARBON	RANGE	ΔE_{vis} KCAL./MOLE	ΔE_{vap} AT 25° KCAL./MOLE	$\frac{\Delta E_{vap} \text{ AT } 25°}{\Delta E_{vis}}$
n-C_5H_{12}	0°–b.p.	1.58	5.71	3.61
n-C_6H_{14}	0°–b.p.	1.73	6.96	4.01
n-C_7H_{16}	0°–b.p.	1.91	8.11	4.25
n-C_8H_{18}	0°–b.p.	2.14	9.21	4.30
n-C_9H_{20}	0°–40°	2.44	10.21	4.20
n-$C_{10}H_{22}$	0°–30°	2.60	11.11	4.28
n-$C_{11}H_{24}$	0°–30°	3.06	11.96	3.91
n-$C_{14}H_{30}$	20°–40°	3.60	14.21	3.95
n-$C_{16}H_{34}$	20°–40°	4.01	15.51	3.87
n-$C_{18}H_{38}$	40°–60°	4.15	16.76	4.03

[9] Colloid Symposium Monograph **3**, 54 (1925).

Water and other associated liquids

Liquids composed of molecules containing OH or NH groups are those ordinarily called abnormal or associated liquids. Among other anomalies they have much higher viscosities than would be expected from the size and internal structure of the molecules. For instance, H_2O is much more viscous than H_2S or CH_4; C_2H_5OH and $C_2H_5NH_2$ are much more viscous than propane; aniline and phenol are more viscous than toluene; etc. This abnormally large viscosity is, of course, due to the hydrogen bond structure of these liquids. When a molecule in such a liquid flows it must not only break van der Waals and dipole "bonds," but also hydrogen bonds. Table VI shows that log η *vs.* $1/T$ is not a straight line for H_2O, but that $\Delta E_{vis}(=Rd \ln \eta/d(1/T))$ decreases rapidly as the temperature increases, and further that the ratio $\Delta E_{vap}/\Delta E_{vis}$ increases with the temperature. Assuming that $n=4$ for water these figures would indicate according to our previous notions that the average unit of flow in water is about two molecules at 0°, and this decreases gradually so that at 150° the average unit of flow is nearly one molecule. A more probable explanation of this behavior is that the single H_2O molecule is the unit of flow at all temperatures, but that when a molecule of water flows the energy of activation for flow is equal to 1/n of the energy of vaporization due to undirected attractive forces (van der Waals and dipole attraction) plus *all* of the energy of vaporization due to *directed* forces (hydrogen bonds). Thus if α is the degree of coordination present in water, i.e., the average number of hydrogen bonds attached to a molecule, we have (neglecting repulsive forces):

TABLE VI.

t°C	η MILLI-POISES	ΔE_{vis} CAL./MOLE	ΔE_{vap} CAL./MOLE	$\frac{\Delta E_{vap}}{\Delta E_{vis}}$	α ($n=4$)	α ($n=6$)
0	17.95	5060	10,180	2.01	2.24	2.68
50	5.49	3420	9,615	2.81	0.92	1.44
100	2.84	2800	8,980	3.20	0.48	1.04
150	1.84	2110	8,280	3.90	0.04	0.60

$$\Delta E_{vap}=\tfrac{1}{2}\Big[\alpha\epsilon_{H-bond}+\sum_{i=2}^{N}\epsilon_{1i}\ \text{(van der Waals)}+\sum_{i=2}^{N}\epsilon_{1i}\ \text{(dipole)}\Big]$$

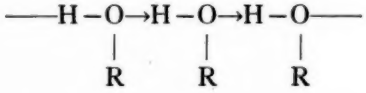
and

$$\Delta E_{vis}=\tfrac{1}{2}\alpha\epsilon_{H-bond}+1/n(\Delta E_{vap}-\tfrac{1}{2}\alpha\epsilon_{H-bond}). \quad (5)$$

Then the rapid decrease of η and ΔE_{vis} with rising temperature is due to the decrease in the number of hydrogen bonds that have to be broken for flow to take place. This activation energy due to hydrogen bonds can be called structure activation energy of flow, and it will be an important factor in any liquid or mixture of liquids containing OH or NH groups. This structure activation energy is the cause of the very high viscosities of glycol, glycerol, sugars, etc., since a three-dimensional network of hydrogen bonds can be formed in these liquids. Lacking hydrogen bonds glycol and glycerol would be expected to have about the same viscosity as butane and 3-methyl pentane, respectively.

If n is assumed to be equal to 4 for water by analogy with other polar liquids (see Table I), and the energy of the hydrogen bond is assumed to be 3000 cal./mole,[10] Eq. (5) can be used to compute the degree of coordination in liquid water at different temperatures. The results are given in column 6 of Table VI. These values of α are undoubtedly low, for n would probably be larger than 4 for water. In an open structure such as water has, a smaller fraction of the energy of vaporization (considering only that portion due to undirected forces) should be sufficient to activate the flow process than in ordinary closer packed liquids. If n is taken as 6, for example, the values of α in column 7 result. This calculation is, of course, very approximate, but it does show the decrease in the degree of coordination with rising temperature. Burnham, Cross and Leighton[10] concluded from Raman spectra that in the range 25 to 90° water is slightly more than two coordinated, which is in approximate agreement with the value of α at lower temperatures in Table VI. It seems likely, however, that α should decrease significantly between 25 and 90°, although possibly not as much as indicated in Table VI.

Similar considerations can be applied to other associated liquids, the maximum possible coordination being twice the number of OH or NH groups in the molecule. Monohydric alcohols would have a maximum coordination of two, and the fact that ethyl alcohol and water have about the same viscosity indicates that ethyl alcohol must possess a large fraction of its maximum two-coordination. Alcohols may be composed of chains



with the R groups arranged roughly parallel in the liquid, or possibly rings containing three or four molecules linked in a similar fashion. Glycol has a maximum coordination of four, the same as water, and the fact that glycol is 20 times as viscous as water indicates that the degree of coordination is much higher in glycol than in water. This is probably due to the fact that the two OH groups are separated in glycol giving less interference between the hydrogen bonds attached to the two groups. Similarly glycerol has a maximum coordination of six, so that as little as half of the maximum coordination will permit a three-dimensional network of hydrogen bonds, giving rise to the very high viscosity of glycerol. Conclusions such as these in this paragraph are necessarily very approximate since the relative contributions to the energy of vaporization of van der Waals, dipole and hydrogen bond forces, and especially of repulsive forces, are not known for any associated liquid. Further work is in progress in an attempt to throw light on this question utilizing viscosity data.

The variation of viscosity with pressure

We have the general relationship that the energy to make a hole the size of a molecule at any pressure is the energy required to take a molecule from the liquid to vacuum. At small pressures the latter energy is the usual energy of vaporization as used in the preceding treatment. The general expression for the energy of making a hole the size of a molecule is however

$$v(p_{int}+p_{ext}),$$

i.e., the work of expanding a volume v against the combined internal and external pressure, where v is the volume occupied by a molecule at p_{ext}, i.e., V/N. At small pressures $Vp_{int}=\Delta E_{vap}$ and Vp_{ext} is negligible compared to ΔE_{vap}. At high pressures, however, Eq. (4) must be written in the more general form:

[10] Burnham, Cross and Leighton, J. Am. Chem. Soc. **59**, 1134 (1937).

$$\eta = 1.090 \cdot 10^{-3} \frac{M^{\frac{1}{2}} T^{\frac{1}{2}}}{V^{5/3}(p_{\text{int}} + p_{\text{ext}})} e^{V(p_{\text{int}} + p_{\text{ext}})/nRT}, \quad (6)$$

where b has again been taken as 2, and n will have the same value for both temperature and pressure variation, at least, for moderate pressures (up to several thousand atmospheres).

If the internal pressure, $p_{\text{int}} = (\partial E/\partial V)_T$, can be evaluated, Eq. (6) can be used to calculate the variation of viscosity with pressure. Or conversely, the experimental values of the variation of viscosity with pressure can be used to calculate the internal pressures, which can then be compared with those derived from other sources. This has been done for several liquids using Bridgman's viscosity-pressure data[11] and compressibility data.[12] The internal pressure at one atmosphere was taken as $\Delta E_{\text{vap}}/V$, and the internal pressures at higher pressures were obtained by trial and error in order to get the experimentally observed relative viscosities (relative to the viscosity at atmospheric pressure). The results for ether and n-pentane (using $n=4$) are shown in the circles of Fig. 3. Also shown are values of the internal pressures calculated from the thermodynamic equation

$$p_{\text{int}} = (\partial E/\partial V)_T = T(\partial p/\partial T)_V - p. \quad (7)$$

The squares are the internal pressures calculated in this way by Hildebrand[13] from Bridgman's earlier compressibility data on ether. The triangles are the internal pressures calculated for ether and n-pentane in the same way from Bridgman's later data.

The internal pressures calculated from the viscosity data lie on a much smoother curve than those calculated from compressibilities, and from the nature of the agreement it is hard to say which is likely to be the most nearly correct set of values. For several other liquids, C_2H_5Br, C_2H_5I, CS_2, all using Bridgman's earlier compressibility data, the agreement was not quite as good, the internal pressures from viscosities being higher than those from compressibilities, particularly at high pressures. In the curves in Fig. 3 the same tendency is also noted at high pressures. If the internal pressures calculated from compressibilities are assumed to be the true ones, this would mean that a little larger fraction of the volume occupied by a molecule is necessary for the elementary process to occur at high pressures where the molecules have been squeezed in closer together. Or in other words, a little higher activation energy is required than that to be expected from the simple picture. When short range forces, such as exchange and dipole forces, come into play, the potential energy ceases to be a function of volume alone and depends on relative orientation. This is exemplified in marked degree in water as discussed in the last section. In such liquids the activation energy for flow depends not only on the fact that a hole is required before the elementary process can take place, but also on the directed bonds to neighbors, since directed bonds to neighbors cannot be made in the relatively disordered activated state. Even normal liquids will at sufficiently high pressures show the same directed potentials arising from exchange interaction, and this may be the cause of the activation energy of flow at high pressures being higher than that given by the simple theory.

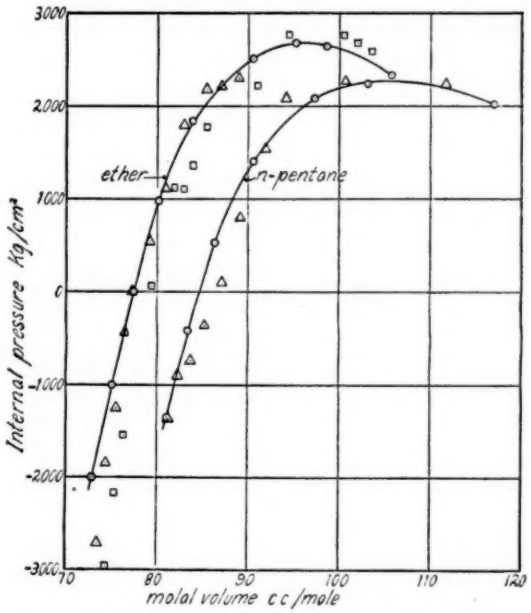


FIG. 3. Plots of internal pressure *vs.* molal volume for ether and n-pentane. The circles are values computed from Eq. (6) using Bridgman's data for viscosity under pressure. The triangles and squares are values computed from Eq. (7) using Bridgman's newer (1931) and older (1914) compressibility data, respectively.

[11] Proc. Am. Acad. Arts Sci. **61**, 57 (1926).
[12] Ibid. **49**, 1 (1913–14); **66**, 185 (1931).
[13] Phys. Rev. **34**, 984 (1929).

TABLE VII. *Approximate calculation of viscosity of as a function of pressure using Eq. (6) and assuming* $p_{int} = \Delta E_{vap}/V$.

	Ethyl Bromide		Ethyl Ether		Carbon Disulfide	
p kg/cm²	(η/η_0) calc.	(η/η_0) obs.	(η/η_0) calc.	(η/η_0) obs.	(η/η_0) calc.	(η/η_0) obs.
1	1.00	1.00	1.00	1.00	1.00	1.00
500	1.29	1.32	1.42	1.55	1.22	1.23
1000	1.63	1.67	1.95	2.11	1.49	1.45
2000	2.62	2.44	3.74	3.27	2.20	2.03

The liquids which have $n=3$, CCl_4, C_6H_6 and cyclohexane, have such low freezing pressures that the viscosities and compressibilities have not been measured above 1500 kg/cm², and this range is insufficient to make a significant test with these liquids.

The calculated internal pressures, $(\partial E/\partial V)_T$, are the slopes of the potential energy-volume curve of the liquid, and they suffice to construct the general features of the potential energy curve. The point where the internal pressure is a maximum, i.e., where

$$\left(\frac{\partial p_{\text{int}}}{\partial V}\right)_T = \left(\frac{\partial^2 E}{\partial V^2}\right) = 0,$$

is the inflection point of the potential energy curve where the repulsive forces are just beginning to become effective. The point where the internal pressure is zero, i.e., $p_{\text{int}} = (\partial E/\partial V)_T = 0$, is the minimum of the potential energy curve. At smaller volumes $(\partial E/\partial V)_T$ becomes a larger and larger negative quantity, corresponding to the rapidly increasing repulsive energy.

The pressure range from atmospheric pressure up to about 2000 kg/cm² includes the broad maximum part of the internal pressure-volume curve, and so in this range of pressures the energy of vaporization measured at atmospheric pressure can be taken as approximately equal to Vp_{int}, and the viscosity as a function of pressure can be computed approximately up to about 2000 kg/cm² using Eq. (6) without requiring any compressibility data, except that required to know the volumes at the particular temperature in question. Table VII shows the results of some calculations at 30°. At pressures higher than 2000 kg/cm² this computation is increasingly poor as the true internal pressure deviates more and more from $\Delta E_{\text{vap}}/V$.

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The Molecular Volumes and Expansivities of Liquid Normal Hydrogen and Parahydrogen

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The molecular volumes at saturation of liquid normal hydrogen and parahydrogen between 14° and 20.4°K were measured with a fused quartz dilatometer, the amount of hydrogen being determined from the pressure of the gas in a calibrated flask at a measured temperature. The results are represented by the equations:

$V(n\text{-}H_2)$ cm³ mole^{-1} $= 24.747 - 0.08005T + 0.012716T^2$,
$V(p\text{-}H_2)$ cm³ mole^{-1} $= 24.902 - 0.0888T + 0.013104T^2$.

At the normal boiling point of n-H_2(20.38°K), $V(n\text{-}H_2) = 28.397 \pm 0.010$ and $\Delta V(p\text{-}n) = 0.138 \pm 0.010$. The expansivity of p-H_2 is only slightly greater than that of n-H_2. The change observed in the molecular volumes of H_2 in passing from the state in which the molecules rotate (o-H_2) to the state in which they do not rotate (p-H_2) is opposite in direction to the change observed in other substances when passing between these two states of molecular rotation and nonrotation. The changes in "lattice" energies are also of opposite sign. It is shown that the random state of orientation of the axes of p-H_2 molecules makes the state of nonrotating p-H_2 fundamentally like that of rotation in other substances at high temperatures. The differences in the molecular volumes and "lattice" energies of the condensed phases of o- and p-H_2 arise from a difference in the magnitude and symmetry of the intermolecular forces of repulsion. These differences in the forces of repulsion result from a difference in the distributions of the average electron density of o-H_2 and p-H_2 molecules arising from the difference in the rotational motion of the two varieties at low temperatures.

Introduction

SOME recent investigations of x-ray diffraction, dielectric constants and specific heats show that the molecules of a number of substances in a condensed phase are oriented. These experiments have shown also that at a certain temperature, characteristic of the material, the oscillatory motion of the molecules about the direction of orientation changes to molecular rotation. This change is accompanied by an increase in molecular volume and in the energy of the condensed phase (hump on the specific heat curve), the state of molecular rotation having the larger volume and larger energy.

In liquid parahydrogen, p-H_2, below 20°K, there is no molecular rotation since practically all the molecules are in the state whose rotational quantum number, j, is 0, whereas in liquid orthohydrogen, o-H_2 ($j=1$) there is "free" molecular rotation which is demonstrated by the fact that the difference in energies of the rotational levels is the same in the liquid and gaseous phases.[1] The variation with temperature of the difference in vapor pressure of these two forms of hydrogen reveals a difference in the "lattice" energies of the condensed state, and one is led to expect a difference in molecular volumes also. The condensed state of o-H has the lower "lattice" energy although it has the greater total energy, and it has now been found that it has also the smaller molecular volume. Thus it is seen that in the case of liquid hydrogen, the change from the state in which the molecules do not rotate (p-H_2) to the state in which they do rotate (o-H_2) is accompanied by a decrease in the molecular volume and "lattice" energy of the condensed state. *This is opposite to the direction of the change in the other substances that have been investigated.* It will be brought out in the discussion that the condensed state of nonrotating p-H_2 is fundamentally like that of molecular rotation in the other substances investigated, the state of rotating o-H_2 corresponding to the state of molecular orientation in other substances.

The measurements were made on normal hydrogen (75 percent o-H_2), and 20.4°K temperature equilibrium hydrogen (99.8 percent p-H_2).[2] Careful measurements of the density and expansitivity of liquid hydrogen had previously been made by Onnes and Crommelin[3] but these measurements were made before the *ortho* and *para* forms of H_2 had been discovered, whereas it is now known that liquid normal H_2 changes at an appreciable rate by conversion of the *ortho* constituent into p-H_2. The molecular volume and expansivity of liquid normal H_2 were, therefore, carefully redetermined. The molecular volume and expansivity of liquid p-H_2 were measured in the same apparatus.

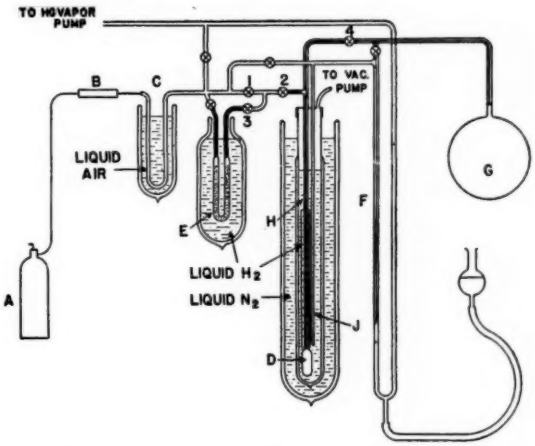

FIG. 1. Diagram of apparatus used to measure the molecular volumes: A, cylinder of hydrogen; B, tube containing copper gauze; C, U-tube containing cotton; D, dilatometer; E, catalyst; F, Hg manometer; G, 3 liter calibrated flask; H, fused quartz capillary; J, vapor pressure tube.

Apparatus and Method of Measurement

The apparatus used is shown diagrammatically in Fig. 1. Electrolytic hydrogen of high purity, containing less than 0.02 mole percent of air, from cylinder A was passed over copper gauze in tube B at 600°C to remove oxygen and insure the normal concentration of the *ortho* and *para* varieties. It then passed through a cotton filter in the U-tube C, which was surrounded by liquid air, to remove water vapor. When measurements were to be made on normal hydrogen, the hydrogen was then allowed to pass through stopcocks 1 and 2 directly to the calibrated fused quartz dilatometer D, of about 3 cm³ capacity. Para-

[1] J. C. McLennan and J. H. McLeod, Roy. Soc. Canada, Trans. **23**, 19–20 (1929).

[2] Harkness and Deming, J. Am. Chem. Soc. **54**, 2850 (1932).

[3] Onnes and Crommelin, Leiden Comm. No. 137a (1913).

TABLE I. *The molecular volume of liquid normal hydrogen at saturation pressure (experimental data).*

DATE	$P(n\text{-}H_2)$† MM Hg	T °K	V_{gas}/V_{liq}† (OBSERVED)	V_{liq} (OBS) CM³ MOLE⁻¹	ΔV_{liq} (OBS−CALC) CM³ MOLE⁻¹
July 15, 1936	749.8	20.34	789.87	28.395	+0.015
"	65.0	14.25	856.71	26.179	−0.009
July 23, 1936	754.1	20.35	790.10	28.386	+0.002
"	65.4	14.26	855.79	26.207	+0.016
"	220.0	16.81	830.67	27.000	+0.005
"	335.3	17.89	819.04	27.383	−0.002
"	518.8	19.15	804.75	27.870	−0.007
"	751.4	20.34	790.00	28.390	+0.010
July 30, 1936	752.4	20.35	790.03	28.389	+0.005
"	81.7	14.67	852.36	26.313	+0.004
"	108.7	15.24	846.72	26.488	+0.008
"	201.8	16.60	832.87	26.930	+0.008
"	308.9	17.67	821.30	27.308	+0.005
"	410.2	18.46	812.79	27.594	−0.009
"	571.8	19.45	800.73	28.009	+0.009
"	751.7	20.34	790.08	28.387	+0.007
August 7, 1936	758.7	20.37	790.20	28.383	−0.010
"	79.5	14.62	853.30	26.284	−0.011
"	111.2	15.29	846.59	26.492	−0.004
"	186.7	16.42	834.94	26.862	+0.001
"	290.7	17.51	823.38	27.239	−0.005
"	450.6	18.73	809.78	27.696	−0.013
"	550.9	19.34	802.64	27.943	−0.012
"	756.9	20.37	790.23	28.382	−0.010

† Corrected for the uncatalyzed *ortho* to *para* conversion of liquid hydrogen.

hydrogen was obtained by condensing hydrogen in the U-tube E containing zinc-chromite, an *ortho-para* conversion catalyst.[4, 5] After allowing it to stand in contact with the catalyst at liquid hydrogen temperatures one and a half to four hours, for complete conversion, the parahydrogen was transferred into the dilatometer by opening stopcocks 3 and 2 and reducing the pressure above the hydrogen bath H by means of a vacuum pump. The molecular volume obtained for parahydrogen was the same whether the hydrogen had been in contact with the catalyst one and a half or four hours, indicating that the conversion to the low temperature equilibrium concentration was complete.

In order to determine the temperature of the liquid hydrogen bath surrounding the dilatometer, normal hydrogen was condensed in the tube J and its vapor pressure was read on manometer F. An electrical heater at the bottom of the liquid hydrogen bath caused boiling and promoted uniformity of temperature.[6] The volume of the condensed hydrogen was determined by reading the position of the liquid meniscus in the tube of the dilatometer by means of a scale fastened to the tube. The flasks surrounding the dilatometer were unsilvered. Reference marks on the fused quartz dilatometer tube provided a means of determining the length of the scale at liquid hydrogen temperature. The volume of the liquid was measured at several temperatures, obtained by adjusting the pressure over the liquid hydrogen bath.

The amount of hydrogen used was determined from measurements of the pressure and temperature of the gas in a flask of known volume. After the measurements of the volume of the liquid in the dilatometer were completed stopcock 4 was opened and the hydrogen allowed to evaporate into flask G. The tube J and manometer F were evacuated and the whole apparatus allowed to warm up to room temperature over night. The next day the pressure of the hydrogen flask G was measured with the manometer F. The flask was surrounded by a stirred, insulated water bath at approximately room temperature. A careful determination of the volume of the flask and con-

[4] H. Diamond, Thesis, Princeton University (1935).
[5] Brickwedde, Scott and Taylor, J. Chem. Phys. **3**, 653 (1935).
[6] In order to be certain that the heater did not raise the temperature of the bulb above that of the bath, a number of volume determinations were made with the heater current turned off during the readings. No difference was observed. However, if the heater was not used at all, superheating of the bath caused random scattering of the results.

necting tubes was made after all other measurements were completed. The volume outside the water bath was only about 18 cm³, the volume of the flask *G* being 3264 cm³. The volume of the hydrogen at 0°C and 1 atmosphere was computed from readings of the pressure in the flask *G* at the temperature of the water bath using the PVT relations for hydrogen given in the *International Critical Tables*, Vol. III, p. 4. A small correction, about 0.2 cm³, was necessary to compensate for the change in volume of the flask with pressure, since the amount of hydrogen used produced a pressure of about 630 mm Hg instead of 1 atmosphere.

The expansion of the fused quartz dilatometer between 20°C and liquid hydrogen temperature was taken as $\Delta V/V=0.000165$ which is the mean of some unpublished measurements of this laboratory on 3 different specimens of fused quartz. A correction had to be made for the hydrogen vapor above the liquid in the capillary tube of the dilatometer. The part of this correction which arises from that section of the tube (0.75 mm bore) extending from the top of the liquid hydrogen bath to the part at room temperature was somewhat uncertain since the temperature along the tube was estimated. However, the correction for this intermediate section amounted to only about 0.012 percent of the final result.

The readings on the vapor pressure of normal hydrogen, from which the temperatures were calculated, were corrected for the uncatalyzed ortho to para conversion of liquid hydrogen, in accordance with measurements made previously of the change in the vapor pressure of hydrogen with time.[7] After the limiting volume of parahydrogen had been determined, a similar correction was made for the change in volume of liquid normal hydrogen with time, which also results from the uncatalyzed *ortho* to *para* conversion.

Results

The molecular volume of the liquid was calculated from the experimentally determined ratios of the volume of the gas to the volume of the liquid, V_{gas}/V_{liq}, using 22,428 cm³ mole^{-1} as the molecular volume of hydrogen at 0°C and 1 normal atmosphere. This value for the molecular volume of hydrogen was computed from the volume of an ideal gas, 22,414 cm³ mole^{-1},[8] at the same temperature and pressure and the value[9] 0.99939 for $1+\lambda$, defined by the equation

$$1+\lambda=\frac{p_0V_0(0°\text{C, 0 Atmos.})}{p_1V_1(0°\text{C, 1}A_n)}.$$

Table I contains the results of the measurements on normal hydrogen. The temperatures given in column 3 were calculated from the corresponding corrected vapor pressures of normal hydrogen, column 2, by means of the following vapor pressure equation, used in previous papers:

$$\log_{10}P(\text{mm Hg})=4.6633-(44.7291/T)+0.02023T. \quad (1)$$

It was found that the volume temperature relations of liquid normal hydrogen and liquid parahydrogen at their respective saturation pressures could be represented by a quadratic equation of the form:

$$V=A+BT+CT^2. \quad (2)$$

[7] Scott, Brickwedde, Urey and Wahl, J. Chem. Phys. **2**, 458 (1934).

[8] Birge, Phys. Rev. Supp. Vol. 1, No. 1 (1929).

[9] *International Critical Tables*, Vol. III, p. 3.

TABLE II. *The molecular volume of liquid parahydrogen at saturation pressure (experimental data).*

DATE	$P(n\text{-}H_2)$† MM Hg	T °K	V_{gas}/V_{liq} (OBSERVED)	V_{liq} (OBS) CM³ MOLE^{-1}	ΔV_{liq} (OBS−CALC) CM³ MOLE^{-1}
August 27, 1936	68.5	14.35	851.82	26.330	+0.004
"	117.9	15.41	841.62	26.649	+0.004
"	221.8	16.83	826.97	27.121	+0.002
"	374.0	18.19	811.86	27.625	+0.002
"	633.7	19.78	793.44	28.267	−0.005
"	754.2	20.36	786.16	28.529	+0.003
August 28, 1936	140.5	15.78	838.33	26.753	−0.009
"	314.7	17.72	817.08	27.449	+0.006
"	567.8	19.43	797.56	28.121	−0.003
"	748.3	20.33	786.57	28.514	−0.003

† Corrected for the uncatalyzed *ortho* to *para* conversion of liquid hydrogen.

The values of the constants A, B and C for liquid normal hydrogen, calculated from the data by the method of least squares, were found to be

$$A = 24.747,$$
$$B = -0.08005,$$
$$C = 0.012716.$$

Column 6, Table I, shows the difference between the observed and calculated volumes of liquid normal hydrogen.

Table II shows corresponding results on parahydrogen. The values of the constants in Eq. (2) representing the molecular volume-temperature relation of liquid parahydrogen, also calculated by the method of least squares, are:

$$A = 24.902,$$
$$B = -0.0888,$$
$$C = 0.013104.$$

Table III gives the molecular volume and expansivity $(1/V_{20.38})(dV/dT)$ at saturation pressure, of normal and parahydrogen, calculated from Eq. (2). The densities of n-H_2 and p-H_2 (Table III) were calculated from the molecular volumes and the molecular weight of H_2. The molecular weight of hydrogen containing the normal amount (D/H = 1/6500) of deuterium is 2.0161 grams.[10] The molecular weight of pure protium hydrogen (H_2^1) is 2.0158 so that the densities of liquid protium hydrogen are 3 parts in 20,000 less than the densities of naturally occurring hydrogen.

Column 8 shows the difference in molecular volumes of *para* and normal hydrogen. It is seen that at the normal boiling point of normal hydrogen the molecular volume of parahydrogen is about 0.138 cm^3 $mole^{-1}$, or 0.49 percent, greater than that of normal hydrogen. The values given in column 9 are the differences in expansivities of *para* and normal hydrogen. The error in these differences in expansivities may be large since their values represent a small difference of two derivatives. They are to be regarded only as indicating the direction and order of magnitude of this difference. The difference in density of normal and parahydrogen is almost constant (column 4–column 7). At 20.38°K this difference is 0.00034 g cm^{-3} and at 14.00°K it is 0.00032 g cm^{-3}. The change 0.00002 g cm^{-3} is of the order of magnitude of the probable error of the results.

In estimating the probable error of the results, the deviations of the observed volumes from Eq. (2) were taken as a measure of that part of the probable error due to accidental errors of observation. This was estimated at ±0.02 percent, somewhat less than the mean deviation of the observations. In addition, systematic errors of measurement were considered. The sources of these systematic errors and their probable magnitudes follow:

(1) An error in the determination of the volume of that part of the apparatus in which the amounts of gas were measured: 0.01 percent.

(2) An error in the determination of the amount of vapor above the liquid in the dilatometer: 0.01 percent.

(3) An error in the correction of the liquid volume and vapor pressure of normal hydrogen for the uncatalyzed *ortho* to *para* conversion: 0.01 percent.

[10] The atomic weight of naturally occurring hydrogen (1.00805) used in this paper is based on the mass-spectrograph results of Aston and Bainbridge, and the latest values of the relative abundances of the isotopes of hydrogen and oxygen. See F. W. Aston, Nature **137**, 357 (1936); K. T. Bainbridge and E. B. Jordan, Bulletin of Amer. Phys. Soc. **11**, 18 (1936); Manian, Urey and Bleakney, J. Am. Chem. Soc. **56**, 2601 (1936); N. T. Hall and T. O. Jones, J. Am. Chem. Soc. **56**, 1915 (1936). The value used for the abundance of $O^{17} : O^{16} = 0.0004 : 1$.

TABLE III. *Molecular volumes, coefficients of expansion, and densities of liquid normal and parahydrogen at saturation pressure.*

	Normal Hydrogen			Parahydrogen			Differences (*Para* − Normal)	
T °K	V cm^3 $mole^{-1}$	$\frac{1}{V_{20.38°K}}\frac{dV}{dT}$ $(°K)^{-1}$	ρ g cm^{-3}	V cm^3 $mole^{-1}$	$\frac{1}{V_{20.38°K}}\frac{dV}{dT}$ $(°K)^{-1}$	ρ g cm^{-3}	ΔV cm^3 $mole^{-1}$	$\Delta\frac{1}{V_{20.38°K}}\frac{dV}{dT}$ $(°K)^{-1}$
20.38	28.397	0.01543	0.07099	28.535	0.01561	0.07065	0.138	0.00018
20.00	28.232	0.01509	0.07141	28.368	0.01526	0.07107	0.136	0.00017
19.00	27.816	0.01420	0.07248	27.945	0.01434	0.07214	0.129	0.00014
18.00	27.426	0.01330	0.07351	27.549	0.01342	0.07318	0.123	0.00012
17.00	27.061	0.01241	0.07450	27.179	0.01250	0.07417	0.118	0.00009
16.00	26.721	0.01151	0.07545	26.836	0.01158	0.07512	0.115	0.00007
15.00	26.407	0.01062	0.07634	26.518	0.01066	0.07602	0.112	0.00004
14.00	26.119	0.00972	0.07719	26.227	0.00975	0.07687	0.108	0.00003

TABLE IV. *Comparison of results of different observers at the normal boiling point of normal hydrogen.*

OBSERVER	DATE	METHOD USED	DENSITY OF LIQUID n-H_2 G CM^{-3}	MOLECULAR VOLUME OF LIQUID n-H_2 CM^3 $MOLE^{-1}$
Dewar	1904	Comparison of volumes of liquid and gas	0.07002	28.79
Onnes and Crommelin	1913	do	.07086	28.45
Augustin	1914	Weighing a sinker in liquid hydrogen	.07097	28.41
Scott and Brickwedde	1937	Comparison of volumes of liquid and gas	.07099	28.397

(4) An error in the determination of the volume of the dilatometer: 0.005 percent.

(5) An error caused by a nitrogen impurity in the hydrogen used: 0.0008 percent.

Considering all of the accidental and systematic errors, the probable error of the results is found to be about ± 0.03 percent. The molecular volumes of liquid normal and parahydrogen *at the normal boiling point of normal hydrogen* (20.38°K according to Eq. (1)) may then be given as:

$$V(n\text{-}H_2) = 28.397 \pm 0.010 \text{ cm}^3 \text{ mole}^{-1},$$
$$V(p\text{-}H_2) = 28.535 \pm 0.010 \text{ cm}^3 \text{ mole}^{-1}.$$

The difference between the molecular volumes of *para* and normal hydrogen, while it is not affected by systematic errors of measurement, includes the accidental errors of two different sets of observations, hence the probable error in the difference is also about ± 0.010 cm^3 $mole^{-1}$. Accordingly the difference in the molecular volumes of p-H_2 and n-H_2 at the normal boiling point of normal hydrogen is given as:

$$\Delta V(p.H_2 - n.H_2) = 0.138 \pm 0.010 \text{ cm}^3 \text{ mole}^{-1}.$$

In Table IV the results of our measurements of the molecular volume of liquid normal hydrogen are compared with values calculated from the density of liquid hydrogen as reported by other investigators. Dewar's[11] value is much the highest. He measured the volume of gaseous hydrogen in a bell-jar gas holder. It is possible that errors in the measurement of volume and temperature of the gas resulted in his high value.

Onnes and Crommelin[3] made careful measurements, and the difference between their value and that reported in this paper is too great to be accounted for by ordinary errors of observation. The existence of *ortho* and *para* varieties of hydrogen was not known at that time and it is probable that their sample of hydrogen contained an excess of parahydrogen. Evidence to this effect is the fact that their value lies between the values reported here for normal and parahydrogen and is somewhat closer to that for normal hydrogen. Although the method of preparation of their hydrogen is not described in the paper[3] on the density, an earlier communication[12] describes a method of preparation of pure hydrogen by means of two distillations of liquid hydrogen, the hydrogen thus obtained to be used "for the replenishment of thermometers and piezometers." This method would result in a high concentration of parahydrogen, both because of the *ortho* to *para* conversion with time and the fractional separation upon distillation. The measurements of Onnes and Crommelin were made over a range of temperatures, making it possible to calculate coefficients of expansion from their data. At the normal boiling point of normal hydrogen the coefficient of expansion determined from their data is 0.0157 $(°C)^{-1}$ as compared with our value of 0.0154 $(°C)^{-1}$.

Augustin[13] gives the density of liquid hydrogen boiling at a pressure of 745.5 mm Hg as 0.07105 g cm^{-3}. Allowing for expansion, this becomes 0.07097 g cm^{-3} at the normal boiling point of normal hydrogen. Augustin's value agrees very well with ours but this agreement is probably fortuitous since his individual determinations, four in number, range as much as 0.00013 g cm^{-3} above and below the mean value reported.

THEORETICAL CONSIDERATIONS

As was pointed out in the "Introduction," the sign of the difference in the lattice energies and molecular volumes of the rotating and nonrotating varieties of H_2 in a condensed phase is oppo-

[11] Dewar, Proc. Roy. Soc. **A73**, 251 (1904).

[12] Onnes, Leiden Comm. No. 94e, p. 59 (1905).

[13] Augustin, Ann. d. Physik **46**, 419 (1915).

site to the sign of the change observed in other substances when passing through the transition from the state of molecular orientation to the state of molecular rotation. The Heisenberg uncertainty principle when applied to the problem of a nonrotating molecule oscillating about a direction of molecular orientation ($\Delta\theta \cdot \Delta[I\theta] \sim h$) shows that for large amplitudes of oscillation, up to 90°, the zero-point energy of the oscillatory motion is of the order of the energy of the rotational level $j=1$, and for smaller amplitudes the zero-point energy is even larger. Because of the small moment of inertia of the H_2 molecule this zero-point energy for an oscillatory motion of p-H_2 molecules would be large, of the order of 300 calories or more. The Raman spectrum of hydrogen arising from transitions between rotational levels is the same for the gaseous and liquid phases[1] to within the accuracy of the measurements showing that the rotational states are characterized by practically the same energy differences in the gaseous and liquid states. This makes it appear unlikely that liquid p-H_2 could have a large zero-point oscillatory energy, and hence the directions of orientation of the axes of the nonrotating p-H_2 molecules in both the liquid and solid phases must be randomly distributed. In this respect of randomness of orientation of the axes of molecules, the state of nonrotating p-H_2 is like that at high temperatures in other substances whose molecules are rotating, since for large rotational quantum numbers the distribution of the axes of the rotating molecules is practically uniform.

The axes of rotation of the o-H_2 molecules in the liquid and solid phases are oriented. At temperatures below the critical point of hydrogen (33°K), practically all o-H_2 molecules are in the state $j=1$, and the three possible orientations of the axis of rotation of an o-H_2 molecule in liquid or solid hydrogen are characterized by the quantum numbers $m=0, \pm 1$. At 0°K all the o-H_2 molecules are concentrated in the state of orientation (m state) having the lowest energy, and in the temperature range below 12°K, in which the specific heat of solid o-H_2 exceeds that of solid p-H_2,[14] molecules are being raised to the m states of higher energy. In the liquid and solid phases, the orientations of the axes of the o-H_2 molecules are not randomly distributed in all possible directions as in the case of p-H_2, hence, o-H_2 corresponds more nearly with other substances at low temperatures where their molecules are oriented and do not rotate, than with these substances at high temperatures where the molecules rotate.

The difference in molecular volumes of the condensed phases of o- and p-H_2 arises from a difference in the intermolecular forces. To the difference in intermolecular forces must also be attributed the difference in "lattice" energies responsible for the differences in vapor pressures of the *ortho* and *para* varieties. It is expected that the van der Waals attractive forces will be nearly the same for o- and p-H_2 since these forces arising from "orbital" electron resonance in neighboring molecules are not really much influenced by molecular rotation. However, the intermolecular forces of repulsion, which arise from the repulsion of regions of high electron density in neighboring molecules, must be different for o- and p-H_2 since their distributions of electron charge density are different. It is then this difference in the distribution of the average electron charge density that is responsible for the differences in molecular volume and vapor pressure.

Not only is there a difference in the magnitude of the intermolecular forces of o- and p-H_2 but, there is also a difference in the symmetry, that is dependence on the angle, of the forces. In liquid and solid o-H_2 the axes of rotation of the o-H_2 molecules are oriented. The forces of molecular orientation in o-H_2 arise from the nonspherical character of the average electron density of the rotating hydrogen molecule. The dependence of the electron density on the polar angle for the rotational state characterized by the quantum numbers j, m, is given by the square of the associated Legendre polymonial $P_{j,m}(\cos\theta)$ which expresses the dependence on θ of the Ψ-function for the diatomic rotator.[15] For p-H_2, $j,m=0,0$, $(P_{0,0})^2=1$; for o-H_2, $j,m=1,0$, $(P_{1,0})^2=\cos^2\theta$ and for o-H_2, $j,m=\pm 1$, $(P_{1,1})^2=\sin^2\theta$. Thus the elec-

[14] Simon, Mendelssohn and Ruhemann, Zeits. f. physik. Chemie **B15**, 121 (1931). Also A. Farkas, *Orthohydrogen, Parahydrogen and Heavy Hydrogen* (Cambridge University Press, 1935), pp. 35–37.

[15] See Ruark and Urey, *Atoms, Molecules and Quanta* (McGraw-Hill Book Co., 1930), pp. 527–531; also A. Farkas, reference 14, pp. 5–7.

tron distribution of p-H_2 at low temperatures is spherically symmetrical and no forces of orientation arise. For the o-H_2 state of lowest energy, $j,m=1,0$, the electron distribution is densest along the polar axis, whereas for the states, $j,m=1,\pm1$ it is densest over the equatorial plane. It is to be expected, therefore, that as the population of the three m states of o-H_2 changes, the forces of orientation will also change.

The average electron distribution for the three m states of o-H_2 ($j=1$) is uniform over all directions as is seen by normalizing the Ψ-functions for the three m states and adding. Therefore, above about 12°K the average electron distribution of all the o-H_2 molecules is uniform like that characteristic of p-H_2 ($j=0$). At any instant, however, an individual o-H_2 molecule is in only one of the three m states so that its electron distribution is not uniform but is that characteristic of its quantum number m at that instant. Even at temperatures above 12°K, then, there is a difference between the electron distributions of the individual *ortho* and *para* molecules. It is to this nonuniform electron distribution of the individual o-H_2 molecules that is attributed the differences between the intermolecular forces and properties of the condensed states of o- and p-H_2 above 12°K.

From the difference between the specific heats of solid o- and p-H_2, it is possible to determine the magnitude of the force of orientation in solid o-H_2. In an o-H_2 crystal whose molecules are all in the state $j,m=1,0$ the molecules will orient themselves so that their angular velocity vectors are aligned perpendicular to the principal axis of the hexagonal crystal. The potential of the orienting force may be represented to a first approximation by the equation $V=V_0(1-\cos 2\theta)$ $=2V_0\sin^2\theta$. In the presence of a force of molecular orientation given by this equation the energies of the states, $j,m=1,\pm1$ are greater[7] than the energy of the state, $j,m=1,0$ by $(4/5)V_0$. The value of V_0 calculated from the difference between the specific heat of solid, 100 percent p-H_2 and the specific heat of solid mixtures of o- and p-H_2[14] at 7°K is about 14 cal. mole^{-1}. The value of V_0 calculated from the difference in specific heats at higher temperatures is smaller (9 cal. mole^{-1} at 10°K). This difference is in agreement with a change expected in the forces of molecular orientation as the population of the three m states changes.

It seems probable that the mutual repulsion of regions of high electron density will permit a closer packing of o-H_2 molecules with high electron density along a line ($m=0$), than o-H_2 molecules with high density over a plane ($m=\pm1$). This makes the o-H_2 state $j,m=1,0$ the low energy state of o-H_2 stable at 0°K as was assumed in the preceding paragraph rather than either of the states $j,m=1,\pm1$. The specific heat data are in accord with this as will now be shown. The angular velocity vectors of the molecules in a crystal of o-H_2 all in the states, $j,m=1,\pm1$ would be directed along the principal axis of the hexagonal crystals so that the potential of the orienting force could be represented to a first approximation by the equation $V=V_0(1+\cos 2\theta)$ $=2V_0\cos^2\theta$. For this case we find that the energy of the state $j,m=1,0$ is greater than that of the states $j,m=1,\pm1$ by $(4/5)$ V_0 which leads to a maximum value of 0.48 cal. °K^{-1} (mole of o-H_2)$^{-1}$ for the difference between the specific heats of solid p-H_2 and a solid solution of o-H_2 and p-H_2 assuming V_0 is independent of the temperature. The experimentally measured specific heat of a solid solution containing 50 percent o-H_2 exceeds that of solid p-H_2 at 5°K by 0.79 cal. °K^{-1} (mole of o-H_2)$^{-1}$ and at this temperature, the lowest reached in the calorimetric experiments, the difference is increasing toward lower temperatures. It seems more reasonable that the low energy state of o-H_2 is the state $j,m=1,0$, than that this difference in specific heats is to be attributed to the rapid rate of decrease of V_0 with temperature (larger than 8 cal. °K^{-1} (mole of o-H_2)$^{-1}$) needed to account for it if the low energy state is $m=+1$ or -1.

It is customary to represent graphically the intermolecular forces in a condensed phase by the "lattice potential energy curve" and to use this curve in demonstrating in a qualitative manner properties of the condensed phase. If the van der Waals attractive forces are very nearly the same for o- and p-H_2, the potential energy curves of the *ortho* and *para* varieties coincide at large values of the distance between the molecules (Fig. 2). The repulsive forces are different for o- and p-H_2 and the two curves deviate from each other at small intermolecular separations. The nearly

equal expansivities and specific heats above 12°K of solid and liquid *o*- and *p*-H_2 are in accord with the similar shapes of the two curves. Actually the expansivity of *p*-H_2 is slightly larger than that of

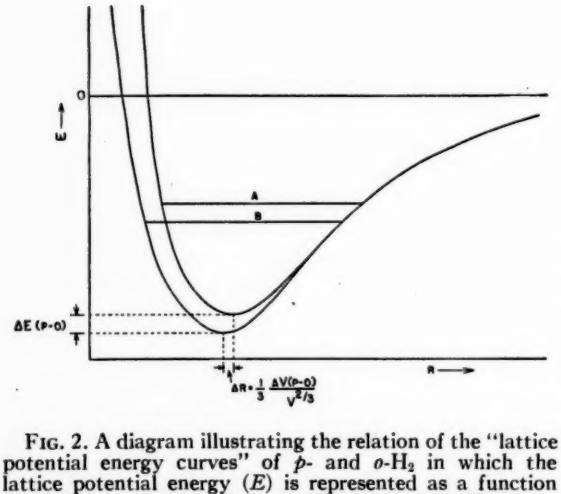

FIG. 2. A diagram illustrating the relation of the "lattice potential energy curves" of *p*- and *o*-H_2 in which the lattice potential energy (E) is represented as a function of the intermolecular distance (R) as abscissa. The horizontal lines A and B represent the lattice energies, kinetic and potential, of *p*- and *o*-H_2 at some temperature, the same for both *p*- and *o*-H_2. This figure is not drawn to scale.

o-H_2, and this difference is in the direction to be accounted for by the two curves as represented in Fig. 2.

At 0°K, at which temperature the *o*-H_2 molecules are concentrated in the state $m=0$, it is probable that the force of orientation is most intense and the difference in molecular volume of the *ortho* and *para* varieties is largest. In the temperature range in which the population of the states $m=\pm 1$ is changing rapidly, the difference in molecular volumes and the relative positions of the potential energy curves will change most rapidly. As the temperature is raised above 12°K, the increasing thermal agitation will interfere to a greater and greater extent with the alignment of the *o*-H_2 molecules, and the potential energy curve of *o*-H_2 will move towards that of *p*-H_2. For solutions of *o*-H_2 and *p*-H_2, the average potential energy curve will lie between those of its pure constituents, its exact position and the forces of orientation depending upon the concentration.

It was shown in a previous paper[5] that the vapor pressure of the nonrotating *o*-D_2 is greater than that of the rotating *p*-D_2 and in this respect *o*-D_2 corresponds to *p*-H_2. It was further demonstrated that the *ortho-para* vapor pressure difference of D_2 is comparable in magnitude with that of H_2. Hence it is expected that there is a difference in the molecular volumes of *o*-D_2 and *p*-D_2 comparable in magnitude with the difference in molecular volumes of *p*-H_2 and *o*-H_2, the molecular volume of *o*-D_2 being greater than that of *p*-D_2.

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The Lattice Energy of Solid CO_2

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It is possible to account for the measured sublimation heat of solid CO_2 by calculating the attraction energy according to London's theory of van der Waals forces; or, when the second approximation of the attractive forces is included, by considering also the electrostatic energy due to the dipole moments and the repulsive energy, the latter being deduced from the equilibrium condition. For the calculation of the electrostatic energy the picture of point charges with definite distances seems preferable to that of short dipoles.

IN the course of other investigations we became interested in the question as to what extent an application of the London theory of van der Waals forces and the present representation of repulsion forces would account for the lattice energies of molecular lattices with linear triatomic molecules such as CO_2 and N_2O. These substances crystallize in cubic face-centered lattices, a type which has been treated by London[1] for simple diatomic molecules. A very rough orienting calculation by treating the molecules as if concentrated in one point, gave the right order of magnitude for the sublimation heats which represent the lattice energies. The values which we obtained for CO_2 will be given in Table I in connection with the more exact calculations.

Calculation in First Approximation

The CO_2 gas crystallizes at very low temperatures in a cubic face-centered lattice, as mentioned above, with the following distances: C−C distance between nearest neighbors $g=3.917$A, C−O distance in one molecule $f=1.12$A and C−C distance between neighbored corners of the cube $a=5.54$A.[2] Those molecules CO_2 located with their C atoms in the corners of the cube point in the direction of the diagonal going through the centers of the cubes. They are all parallel to each other. Those molecules, however, which are located with their C atoms in face centers point to the centers of the edges of the cube. (See Fig. 1.)

London has derived a simple expression for the energy of a molecular lattice considering only dipole-dipole interactions:

$$\Phi=-\frac{CN_L}{2}\sum_i\frac{1}{R_i^6} \quad \text{with} \quad C=\tfrac{3}{4}\alpha^2h\nu, \qquad (1)$$

where N_L is Loschmidt's number, R_i are the distances from one fixed atom to all the other atoms in the lattice, α the polarizability of the atom and $h\nu$ a characteristic energy amount, which corresponds to the principal specific frequency ν taken from the dispersion equation of the particle in question (or about the ionization energy if the dispersion equation is not known). We extend the summation over the distances smaller than the edge of the unit cube calculating the rest by integration.

In the case of CO_2 it seemed plausible to assume that practically only the O atoms contribute to the polarizability, the α value for the C atom in the center being much smaller than for the O atoms.[3] It seems furthermore plausible that in this two-center model for the CO_2 molecule the polarizability of the centers should not be located in the nucleus of the O atoms but should be a little shifted toward the C atom. For this shift there are several assumptions possible which are all more or less arbitrary. In order to remove this arbitrariness we have applied Silberstein's[4] theory to our model although we are aware that this theory is not ideal. But besides removing the arbitrariness of locating the polarizabilities, Silberstein's theory has the other advantage of taking into account

[1] F. London, Zeits. f. physik. Chemie **B11**, 222 (1930).
[2] W. H. Keesom and I. W. L. Köhler, Physica **1**, 167 and 655 (1934).
[3] See for similar considerations F. V. Lenel, Zeits. f. physik. Chemie **B23**, 379 (1933), p. 390.
[4] See for references, H. A. Stuart, *Molekülstruktur* (1935), p. 185.

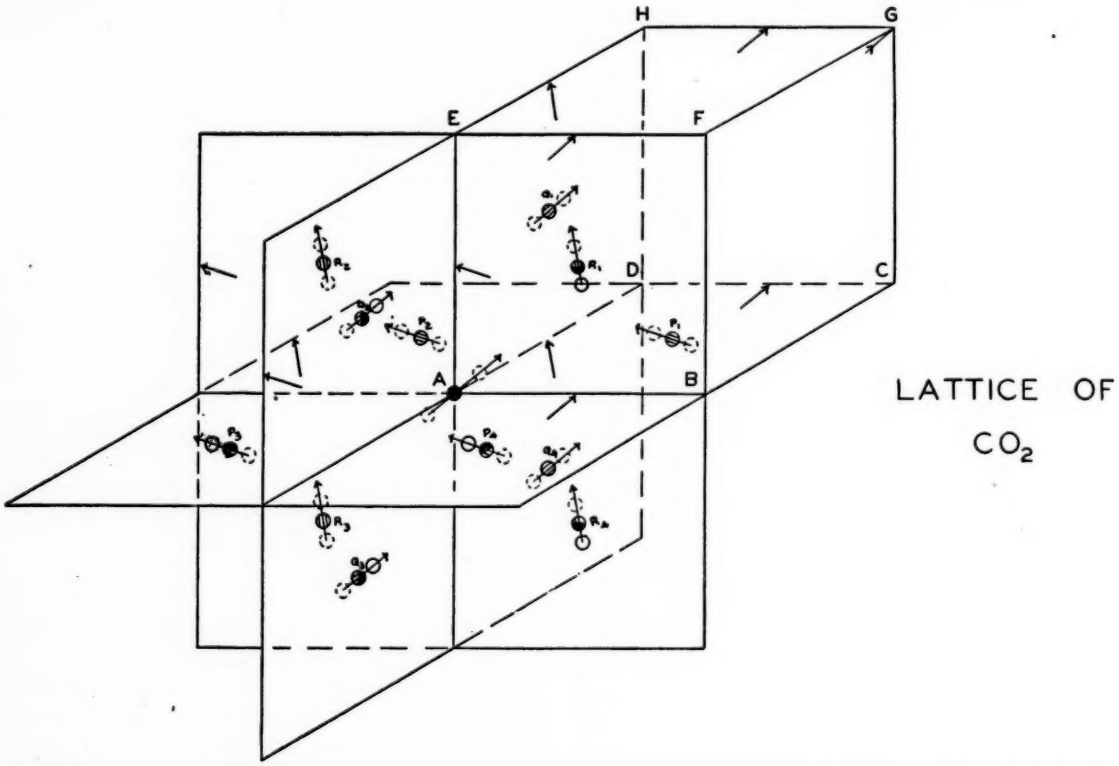

FIG. 1. Arrows show directions of different carbon dioxide molecules. Parallel molecules in same plane are denoted with same letter.

the anisotropy of the polarizability which is 2 : 1 in the case of CO_2. Hence we obtain from Silberstein's theory $r=1.76$A for the distance between the two polarizabilities and $\alpha=1.17\cdot10^{-24}$ for their value. With the described model the distances from the two centers of one fixed molecule A to those of the surrounding 12 molecules in the face centers and to the 6 closest corners of the cubes are shown in the following illustrations.[5] The summation which has been extended from the shortest distance to $r=a=5.54$A gives $\sum(1/R_i^6)=2.74\cdot10^{46}$ cm^{-6}; the integral over the rest, multiplied by the number of centers of attraction per cm^3, gives $0.12\cdot10^{46}$ cm^{-6}. If we now use for the characteristic quantity $h\nu$ in formula (1) the ionization energy[6] of the CO_2 molecule $I=14.4$ ev under the assumption that this is also justified in our two-center model, we obtain a lattice energy of 5.0 kcal./mole whereas the experimental value is 6.44 kcal./mole.[7] One may obtain a figure higher than 5.0 kcal./mole if the specific frequency ν in formula (1) is taken from dispersion data rather than from the ionization potential. The dispersion formula to be used in connection with formula (1) should consist of a single term only. Such a formula has been given by Cuthbertson[8] and has been replaced by Fuchs[9] by a detailed formula containing several terms. We have taken 15.5 ev as characteristic energy for a one term formula and inserting it in London's equation have calculated 5.3 kcal./mole for the lattice energy.

How much we are in error by using the frequencies of the CO_2 molecule for the two

[5] There are 2 molecules with the relative position of A to Q_1, 2 with the relative position of A to P_1, 2 with that of A to Q_2, 2 with that of A to P_2, 4 with that of A to R_1, 6 with that of A to B. The shortest distance between two centers is 2.485A.

[6] This value has been taken from electron impact measurements and hence is to be considered as an upper limit.

[7] Cf. Landolt-Börnstein, *Tabellen*, III. Erg. Band, 3. Teil, p. 2715.

[8] C. and M. Cuthbertson, Proc. Roy. Soc. Lond. **A97**, 152 (1920).

[9] O. Fuchs, Zeits. f. Physik **46**, 519 (1927).

centers of our model cannot be estimated, but we think that the error will not be large because the CO and CO_2 molecules have almost the same ionization potentials and have absorption spectra in the same far ultraviolet region. We have furthermore used London's dispersion formula in connection with Fuchs' dispersion equation for CO_2.[10] Here no α value need be known, the dispersion data being sufficient to build up the attractive force. But we neglect in this case the existence of an anisotropy of the polarizability which will make our calculated value larger than it actually is. Since the knowledge of α is not necessary we have not used here Silberstein's theory at all but have estimated the positions of the two centers in the following rather arbitrary way. We located namely the center of gravity of the negative charges in the same way as L. Meyer[11] has located the binding moment. This is not unreasonable, as the electrons which contribute to the binding moment are part of the dispersion electrons. Thus we placed the centers $\frac{3}{4}f=0.84$A apart from the C atom. Calculation gives now 6.6 kcal./mole for the lattice energy.

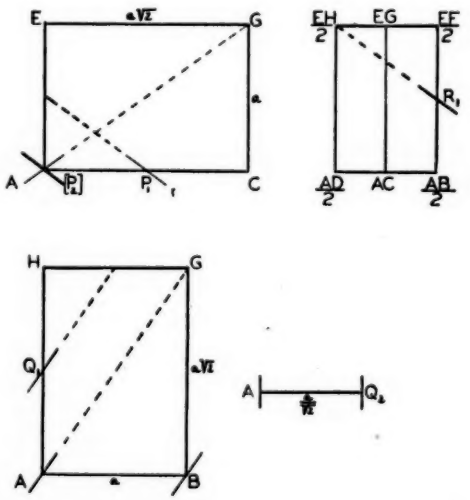

FIG. 2. The brackets indicate that P_2 lies $a/\sqrt{2}$ above the plane of drawing.

[10] The dispersion equation of Fuchs is based upon empirical data in the infrared and in the region from 6000 to 2000A. But since the first principal term contains 720.4A as wave-length of the main frequency, the extrapolation seems rather wide. The observed absorption in the region of 720A is strong and mainly discontinuous.

[11] L. Meyer, Zeits. f. physik. Chemie **B8**, 27 (1930).

Finally we have carried through the calculation of the lattice energy with a location of the two centers of attraction as in the case of the dispersion formula, but using again formula (1) and at the same time half of the mean value of α for each center, i.e., $\alpha/2=13.25\cdot10^{-25}$. This model gives a lattice energy of 5.9 kcal./mole when using the ionization potential of 14.4 ev and 6.3 kcal./mole when using $h\nu=15.5$ ev. Both values would be lowered if the anisotropy of the polarizability would be taken into account.

Summarizing we see that the lattice energies for our model lie between 5.0 and 6.6 kcal./mole with probably the best value of 5.3 kcal./mole.

Second Approximation of the Attraction Energy

For the second approximation Margenau[12] has given a formula of the dipole-dipole and dipole-quadrupole interaction. The formula contains mean values of powers of the distance of the electrons from the nucleus. Expressing them with the help of the polarizability and the characteristic energy and neglecting thereby the different ways in which the average was taken, we can write the total attraction energy in the form:

$$\Phi=-\tfrac{3}{4}h\nu\alpha^2\frac{N_L}{2}\left(\sum_i\frac{1}{R_i^6}+\frac{9\alpha h\nu}{2e^2}\sum_i\frac{1}{R_i^8}\right), \quad (2)$$

where e is the elementary charge. The results for our different models are shown in Table I; the second term amounts to 52–56 percent of the first. (In Margenau's calculation for hydrogen and helium where he used the actual distribution function of the electrons instead of introducing α, the second term amounted to 25–50 percent of the first.)

Other Methods of Calculating the Attraction Energy

For comparison, we have also used a formula derived by Slater and Kirkwood[13] with a different method:

$$\Phi=-163\cdot10^{-12}n^{\frac{1}{2}}\alpha^{\frac{1}{2}}\frac{N_L}{2}\sum_i\frac{1}{R_i^6}, \quad (3)$$

[12] H. Margenau, Phys. Rev. **38**, 747 (1931).

[13] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

where n is the number of electrons in the outer shell (here $n=8$ for each of the two centers), the other letters having the same meanings as noted earlier. It is very difficult to estimate how reliable this method is, as already London[14] has pointed out. The results are included in Table I. They are of the same order of magnitude as those obtained with London's formula including the dipole-quadrupole interaction (although they do not contain this term, which should still be added[15]) and much higher than the experimental value. A still larger value is obtained when using Kirkwood's[16] formula. This can be understood from the fact that this formula can approximately be reduced to the above-mentioned Eq. (3) with the only change that n then means the total number of electrons in the system considered. Hellmann's method[17] would give a value lying between those obtained with the last two methods, for he takes all electrons into consideration, but with a different parameter for each shell and taking into account the Pauli principle.

We have not used these values in further considerations because they are still larger than the one obtained from Slater and Kirkwood's method.

Electrostatic Energy

CO_2 has two dipoles compensating each other. Their moment has been estimated by Smallwood[18] from infrared dispersion data as $\mu=1.2\cdot10^{-18}$ e.s.u., by Lenel[3] from measurements of adsorption heats of CO_2 on crystals of KCl and KJ being $\mu=1.8\cdot10^{-18}$ e.s.u. Smallwood's method is in principle only capable to determine the change of μ with vibration; Lenel's method, although correct in principle, is based upon rough estimation which can only give the order of magnitude. Hence both figures do not represent final values, but they very likely give the right order of magnitude. In order to calculate the electrostatic energy terms connected with these dipoles, one has to make an assumption about their position and their length. Adopting the usual picture of dipoles as point charges with negligible distances and locating them at $f=0.84$A as would follow from Meyer's conceptions,[19] we have applied the ordinary dipole formula[20] $(\mu^2/R^3)(-2\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos\varphi)$ with the result that a repulsion of $\mu^2\cdot1.52\cdot10^{36}$ kcal./mole should be present. Inserting $\mu=1.8\cdot10^{-18}$ a value of 4.9 kcal./mole results, whereas with $\mu=1.2\cdot10^{-18}$ e.s.u. 2.2 kcal./mole are obtained. The first value seems impossible and the second improbable. The results indicate that the distances within our lattice are not large enough to justify the application of the dipole formula. As soon as we locate the dipoles halfway between the C and O atoms on both sides and thus increase the distances between the dipoles in different molecules we obtain the much smaller values of 1.3 and 0.6 kcal./mole, respectively (corresponding to $\mu^2\cdot0.4\cdot10^{36}$ kcal./mole).

But we believe that the charge distribution is much better described with a model of point charges than with dipoles. We have represented it in a very simplified way by means of expressions like

$$\frac{N_L}{2}\epsilon\sum_i\frac{\epsilon_i}{R_i},$$

[14] F. London, Trans. Faraday Soc. **33**, 8 (1937), especially p. 16 and 44.

[15] In an abstract Ch. H. Page (Phys. Rev. **51**, 1002 (1937)) has very recently calculated the second approximation for the Slater-Kirkwood formula in the case of He and finds an increase of 13 percent when compared to Margenau's 26 percent in this special case; but, as he added when presenting the paper at the Meeting of the Am. Phys. Soc. in Washington, Apr. 29, 1937, the dipole-dipole term becomes simultaneously smaller when the series is expanded. The result is then that the total energy is increased only by 1 percent. If this result should be capable of a generalization and hence could be applied to our case, the result of the variation method would be the same as that of London's method including the second approximation.

[16] J. G. Kirkwood, Physik. Zeits. **33**, 57 (1932); A. Müller, Proc. Roy. Soc. Lond. **A154**, 624 (1936).

[17] H. Hellmann, Acta physicochim. U.S.S.R. **2**, 273 (1935); **1**, 913 (1935); J. Chem. Phys. **3**, 61 (1935).

[18] H. M. Smallwood, Phys. Rev. **41**, 164 (1932).

[19] Different authors combine different conceptions with a given dipole moment. Taking, for instance, the dipole moment of the C−Cl bond, $\mu=1.5\cdot10^{-18}$, L. Meyer pictures it as point charges with negligible distance situated at $f=1.62\text{A}=\frac{7}{8}$ of the distance C−Cl. H. M. Smallwood and K. F. Herzfeld (J. Am. Chem. Soc. **52**, 1923 (1930)) also described it as point charges with negligible distance, but situated at $f=0.77$A, the radius of the C atom, whereas G. C. Hampson and A. Weissberger (J. Am. Chem. Soc. **58**, 2111 (1936)) picture it as consisting of two point charges located in the centers of the C and Cl atoms. The difference in results obtained with the different models depends of course more or less on the special problem.

[20] Where θ_i are the angles between the dipoles and their distance from each other and φ the angle around the distance as axis.

where ϵ is the charge of the "dipole." We realize that it is rather incorrect to use here still the word dipole for charges which are quite a distance apart from each other, but it seems a general custom. We have taken the location of the polarizabilities as position of the negative charges and the C atom as center of the positive charges, this picture being very similar to the one used by Lenel.[3] The summation over the electrostatic terms gives an energy of repulsive nature and of value $\mu^2 \cdot 0.085 \cdot 10^{36}$, when using $f=0.88$A and $\mu^2 \cdot 0.15 \cdot 10^{36}$ when using $f=0.84$A. Combining them with Lenel's value we find 0.2 and 0.5 kcal./mole, respectively, while from combining them with Smallwood's figure we obtain 0.1 and 0.2 kcal./mole. These values are much more plausible than the large figures obtained with the dipole formula since the electrostatic forces should not result in a large repulsion when compared to the other terms which constitute the total energy. Part of the repulsion is of course canceled by an attraction due to influence forces resulting from an interaction between the polarizability of one center and the dipole of another center. But these influence forces do not amount to much since the electric fields produced at the position of one polarizable group by the dipoles of all surrounding CO_2 molecules tend to cancel each other. We have not carried out the actual calculation since the electrostatic forces are already small, but we think that the ratio between electrostatic repulsive and influence forces will be about the same as that given by Lenel from a rather elaborate treatment of the influence forces including the inhomogeneity of the electric field. Here the influence forces are about $\frac{1}{4}$ of the electrostatic forces.

It is perhaps not uninteresting to ask what quadrupole moment of CO_2 would result from our assumptions of the charge distribution. Supposing that the distance from a fixed point is large when compared with the dimensions of the molecule, a quadrupole moment of $2-3 \cdot 10^{-26}$ e.s.u. would result.

Energy of Repulsion

The distance by which the molecules in the lattice remain separated from each other is determined by the equilibrium between attractive and repulsive forces. In the case of CO_2 we have found that the electrostatic forces are of repulsive nature, but they do not represent the principal repulsion. Born and Mayer[21] have expressed the repulsive force which results from the quantum mechanical kinematics of the elementary charges, as an exponential function, so that the mutual energy together with van der Waals attraction forces becomes for our example:

$$\Phi = -\frac{A}{R^6} - \frac{B}{R^8} + f(R) + b\sum e^{-(a_i R)/\rho}, \qquad (4)$$

where the first two terms correspond to the van der Waals attraction, the third to the electrostatic energy including influence forces and the fourth to the repulsion. b and ρ are constants and $a_i R$ the distances written as multiples of a smallest distance R. The constant b can be eliminated from the equilibrium condition which is for temperature 0°K and pressure 0

$$\frac{d\Phi(R_{00})}{dR_{00}} = 0 = \frac{6A}{R^7{}_{00}} + \frac{8B}{R^9{}_{00}} + \frac{df(R_{00})}{dR_{00}} - \frac{b}{\rho}\sum_i a_i e^{-(a_i R_{00})/\rho}. \qquad (5)$$

Born and Mayer have determined R/ρ for the alkali halides with the aid of thermodynamical relations in which the compressibility β and the change in volume with temperature at constant pressure are involved. Keesom and Köhler[22] have determined $(1/V)(\partial V/\partial T)_P = 5.07 \cdot 10^{-6} T$ for temperature ranges between 20°K and 114°K, while Maass and Barnes[23] have measured it near the sublimation point and have found it equal to 0.00128 which is larger than a linear extrapolation of Keesom's value would indicate. The compressibility β has been roughly measured by Bridgman[24] after this paper had been pre-

[21] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).
[22] W. H. Keesom and I. W. L. Köhler, Physica **1**, 655 (1934).
[23] O. Maass and W. H. Barnes, Proc. Roy. Soc. Lond. **A111**, 224 (1926).
[24] We wish to express our sincere thanks to Professor Bridgman that he very kindly made these measurements for us and allowed us to use his results in advance of his own publication. Before we had the value of β we could only compare the calculated attraction energy with the experimental lattice energy and from the difference of the two compute a probable value of β.

sented at the Washington meeting of the American Physical Society. He found $\beta = 2.1 \cdot 10^{-11}$ at the sublimation point $T = 195°K$ as an average value between atmospheric pressure and 2500 kg/cm².[25] Since β is not known for the conditions under which Eq. (5) holds and since an extrapolation of β seems very doubtful, we have used the equilibrium condition for a temperature T and pressure 0 which involves a different equilibrium distance $R_{T,0}$. Born has shown that the lattice energy which can be calculated for these different conditions differs by less than 1 percent. Hence our equilibrium condition is

$$R_{T,0}\frac{d\Phi(R_{T,0})}{dR_{T,0}} = \frac{3VT}{N_L}\left(\frac{\partial P}{\partial T}\right)_V = \frac{3T}{\beta N_L}\left(\frac{\partial V}{\partial T}\right)_P$$
$$= \frac{6A}{R^6_{T,0}} + \frac{8B}{R^8_{T,0}} + R_{T,0}\frac{df(R_{T,0})}{dR_{T,0}}$$
$$- b\frac{R_{T,0}}{\rho}\sum_i a_i e^{-(a_i R_{T,0})/\rho} \quad (6)$$

where T, in our case, is 195°K. Within our limit of precision we may neglect the electrostatic term $f(R_{T,0})$, and furthermore put

$$\sum e^{-(a_i R_{T,0})/\rho} \sim \sum a_i e^{-(a_i R_{T,0})/\rho}$$

and
$$R^2_{T,0}\frac{d^2\Phi(R_{T,0})}{dR^2_{T,0}} = \frac{9V}{N_L\beta},$$

which gives us

$$\frac{R_{T,0}}{\rho} = \frac{\dfrac{7\cdot 6A}{R^6_{T,0}} + \dfrac{9\cdot 8B}{R^8_{T,0}} + \dfrac{9V}{N_L\beta}}{\dfrac{6A}{R^6_{T,0}} + \dfrac{8B}{R^8_{T,0}} - \dfrac{3T}{N_L\beta}\left(\dfrac{\partial V}{\partial T}\right)_P}.$$

Using $(1/V)(\partial V/\partial T)_P = 0.00128$ we obtain $R_{T,0}/\rho = 25.67$ (extrapolation of Keesom's value of $(1/V)(\partial V/\partial T)_P$ would give $R_{T,0}/\rho = 20.74$) and inserting this in Eq. (6) the repulsion term becomes 1.1 kcal./mole (with the extrapolation from Keesom's value 1.7 kcal./mole). Combining this result with our calculation for the attraction energy we see from Table I that we obtain the right order of magnitude for the lattice energy. In fact the figures obtained when using Silberstein's theory are quite close to the experimental value. Of course, our whole theoretical consideration is not accurate enough to allow a decision between the two values.

On account of the rather rough treatment no attempt has been made to calculate small effects, like the energy at zero temperature. The Keesom effect, will not be of importance, because the CO_2 molecules do not rotate in the crystal.

Summary

The above considerations have yielded the interesting result that London's simple theory of van der Waals forces already gives a fair representation of the sublimation heat of the molecular lattice of solid CO_2, indicating that higher approximations, electrostatic and repulsive forces seem to cancel each other. When taking into account these terms a fair agreement between calculated and experimental sublimation heat is obtained. It must be admitted, however, that this is somewhat fortuitous because some simplified assumptions enter the theory. The two-center model itself is an approximation which we consider, however, as a rather good one. Of course, it should be borne in mind that the identification of the optical frequency of the two centers with the frequency of the CO_2 molecule introduces some uncertainty. Besides, we do not know how reliable our application of Silberstein's theory is. It does not work so very well in the case of N_2O which has a lattice very similar to that of CO_2 and very nearly the same lattice energy, furthermore the same number of electrons, but with an anisotropy of the polarizability 3 : 1. Unfortunately there exists such a large variety of possible assumptions in this case on account of the lack of symmetry that

[25] It is perhaps of interest to compare the values of β and $(1/V)(\partial V/\partial T)$ for the few molecular crystals, for which we could find such data, namely $PbCl_2$, $CdCl_2$, and C_6H_6. The data are for $PbCl_2$: $\beta = 3.4 \cdot 10^{-12}$ and $(1/V)(\partial V/\partial T) = 9 \cdot 10^{-5}$; for $CdCl_2$: $\beta = 5.95 \cdot 10^{-12}$ and $(1/V)(\partial V/\partial T) = 7.3 \cdot 10^{-5}$ and for C_6H_6: $\beta = 32.9 \cdot 10^{-12}$ and $(1/V)(\partial V/\partial T) = 35 \cdot 10^{-5}$. $PbCl_2$ is according to H. Braekken (Zeits. f. Krist. **A83**, 222 (1932)) a molecular lattice, whereas $CdCl_2$ and benzene are more layer lattices. We calculated the repulsive energy with a Born-Mayer formula in analogy to CO_2 as 1.8 kcal./mole for benzene, while the attractive energy gives according to London and Margenau 8.6 kcal./mole and 11.3 kcal./mole with the Slater-Kirkwood formula (J. H. de Boer, Trans. Faraday Soc. **32**, 10 (1936)). The experimental value is 10.67 kcal./mole. There are perhaps some other sources of attraction energy not yet considered, which could be more or less nonadditive forces acting in the plane that determines the layers.

TABLE I.

METHOD OF CALCULATION	LATTICE ENERGY (KCAL./MOLE)		
One center of attraction/molecule:			
London's formula	3.6		
2nd approx. London+Margenau	6.0		
Formula of Slater and Kirkwood	5.7		
Two centers of attraction/molecule:	$\alpha=13.25\cdot10^{-25}$ (average value) $f=0.84$A		$\alpha=11.7\cdot10^{-25}$ (Silberstein) $f=0.88$A
	$h\nu=14.4$	$h\nu=14.4$	$=15.5$ ev
London's formula	5.9	5.0	5.3
2nd approx. London+Margenau	9.2	7.6	8.2
Dispersion formula	6.6		
Formula of Slater and Kirkwood	9.6		8.6
Electrostatic energy			
Model of point charges	-0.2 to -0.5		-0.1 to -0.2
Dipole formula	-2.2 to -4.9		
Repulsion energy		-1.1	
Calculated sublimation heat	7.7	6.4	7.0
Experimental sublimation heat	6.44		

no definite conclusions can be drawn. In the case of CO_2, however, it is possible, as we have shown, to account theoretically for the observed value.

Our results obtained with different assumptions and approximations are exhibited in Table I.

We wish to express our thanks to Professor E. Teller of George Washington University for valuable suggestions.

A Thermal Conductivity Method for the Determination of Isotopic Exchanges in the Simpler Gaseous Molecules: Erratum

NELSON R. TRENNER
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(J. Chem. Phys. **5**, 382 (1937))

ON page 386 the sentence: "Our combination consisted of 5000 ohms . . . etc.," should read: "Our combination consisted of 5000 ohms between points *G* and *H* and 8500 ohms between points *E* and *G*."

The Mercury Sensitized Reactions of Methane, Deuteromethanes and the Hydrogen Isotopes: Errata

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(J. Chem. Phys. **5**, 212 (1937))

IN Tables XIII and XIV on page 221 the superscript "*a*," indicating the use of a Cl_2-Br_2 filter, should have appeared *only* on the reaction included in the first line of each table. The second and third line reactions were run using the acetic acid filter.

In Fig. 6 on page 223 the reaction represented by curve *G* should have been included with the *exchange* reactions not with the condensations as indicated.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Raman Spectra of *Di-n*-Butyl Ether and Ethyl Adipate

The Raman spectra of *di-n*-butyl ether and ethyl adipate have been measured by means of apparatus described elsewhere.[1] In the following summary of results, the numbers in parentheses represent estimated intensities on the basis of 10 for the strongest Raman line on the plate, the letter *b* indicates that the line is broad, and the letters *e* and *k* following the parentheses designate excitation by the Hg lines at 4358A and 4047A, respectively:

Di-n-butyl ether: Eastman product; purified by distillation at atmospheric pressure, using an effcient heated column; b.p., 140.5°–141.0°; exposure time, 10 hr.; continuous spectrum, weak; previous data, none; Raman frequencies (cm^{-1}), 283(1)*e*; 338(1)*e*; 842(3)*e*, *k*; 882(1)*e*, *k*; 965(2)*e*, *k*; 1033(2)*e*, *k*; 1069(2*b*)*k*; 1147 (2*b*)*k*; 1233($\frac{1}{2}$)*k*; 1304(4)*e*, *k*; 1458(8)*e*, *k*; 2874(8)*e*, *k*; 2929(8*b*)*e*, *k*, shaded to the red.

Ethyl adipate: Synthesized from adipic acid and ethyl alcohol; purified by distillation at reduced pressure, using a heated column; b.p., 131° at 15 mm; exposure time, 20 hr.; continuous spectrum, weak; previous data, none; Raman frequencies (cm^{-1}), 378(2)*e*; 604(1)*e*; 797(1)*e*; 862(4)*e*, *k*; 927(1)*e*; 1040(2)*e*, *k*; 1113(2)*k*; 1305(3)*e*, *k*; 1458(7)*e*, *k*; 1740(5)*e*; 2880 (4)*e*, *k*; 2942(10)*e*, *k*; 2984(5)*e*, *k*.

The Raman line at 2929 cm^{-1} in *di-n*-butyl ether is definitely shaded to the red and is probably made up of two lines. This may be due to a Fermi resonance interaction between the C−H fundamental and the first overtone of the $-CH_2$ frequency at 1458 cm^{-1}. M. E. High[2] has found three lines in this region for *di-n*-amyl ether, but only two for *di-n*-propyl ether.

The Raman line at 2880 cm^{-1} in ethyl adipate is lower in frequency than lines observed in this band for similar compounds; furthermore, three lines are observed instead of the customary two for such related compounds. It may be that 2880 is the first overtone of the $-CH_2$ frequency at 1458 cm^{-1}. The frequency 2880 cm^{-1} in methyl chloride is interpreted in this manner by Sutherland[3] and Adel and Barker[4] have shown that the reason for its intensity is the resonance between this overtone and the C−H fundamental at 2967 cm^{-1}. Paranjpe and Savanur[5] have ascribed the frequencies 630, 1030, and 1730 cm^{-1} to the $O=\overset{|}{C}-O-$ configuration in organic esters; these frequencies in ethyl adipate are 604, 1040, and 1740, respectively.

The dispersion of the spectrograph was 40A/mm at 4500A. A filter solution of cobalt sulfocyanate was used to weaken the Hg line at 4358A when excitation was by 4047 and a solution of saturated sodium nitrite was used to weaken 4047 when excitation was by 4358. Both solutions effectively absorb the Hg lines below 4000A, while the former considerably weakens the continuous background in the range 4500–5000A.

A study of a series of acetylenic compounds is now in progress, after which it is expected that a more detailed investigation of the Raman spectra of ethers and dibasic acids and their esters will be made.

The authors desire to express their appreciation of a partial support of this investigation by a grant from the Virginia Academy of Science.

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[1] Am. Phys. Teacher. (Now in press.)
[2] Phys. Rev. **38**, 1837–1844 (1931).
[3] *Infrared and Raman Spectra* (Methuen & Co., London, 1935), p. 101.
[4] J. Chem. Phys. **2**, 627–629 (1934).
[5] Indian J. Phys. [8.] **6**, 503–520 (1934).

Errata: Thermodynamics of Gaseous Hydrocarbons: Ethane, Ethylene, Propane, Propylene, *n*-Butane, Isobutane, 1-Butene, *Cis* and *Trans* 2-Butenes, Isobutene, and Neopentane (Tetramethylmethane)

(J. Chem. Phys. **5**, 473 (1937))

The calculated values of the free energy of formation of the various hydrocarbons at 1500°K as listed in Table VI are in error. Certain of the interpolated values are also slightly affected. The corrected values are given below:

TABLE VI. *Values of $\Delta F^\circ/T$ of formation for hydrocarbons in the gaseous state. (Units: cal./deg. mole.)*

T, °K	800	900	1200	1500
Ethane	19.7	23.1	29.9	34.5
Propane	37.0	41.2	49.5	54.9
n-Butane	53.5	58.6	68.5	73.8
Isobutane	55.7	61.0	71.0	76.8
Neopentane	75.8	82.3	94.9	112.2
Ethylene	30.0	28.7	26.1	24.8
Propylene	41.8	41.8	41.9	42.0
1-Butene	58.8	59.5	61.1	62.1
Cis 2-Butene	58.8	59.9	62.1	63.7
Trans 2-Butene	58.2	59.5	61.8	63.6
Isobutene	58.3	59.6	62.1	63.9

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